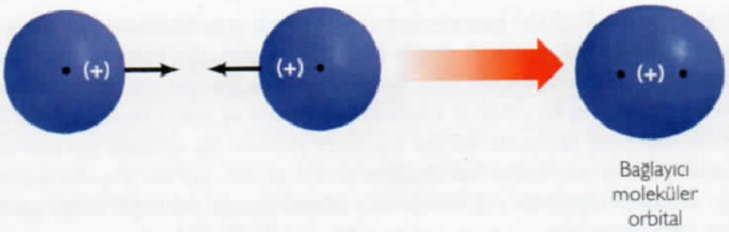
Karbon Bileşikleri ve Kimyasal Bağlar

1.15 KUANTUM MEKANİĞİNDEN ÇIKAN ÖNEMLİ KAVRAMLARIN BİR ÖZETİ

1. **Atomik orbital (AO)** tek bir atomun çekirdeği etrafındaki uzayda, elektronun bulunma olasılığının yüksek olduğu bir bölgeye karşılık gelir. *s* Orbitalleri denen atomik orbitaller küreseldir, *p* orbitalleri denenler ise yaklaşık tanjant küresel şekildedir. Orbitaller spinleri eşleşmiş en çok iki elektron bulundurabilirler. Orbitaller bir dal-

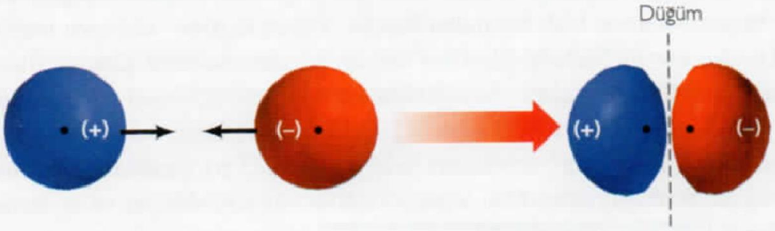
ga fonksiyonu, ψ ile tanımlanırlar ve her bir orbitalin kendine özgü bir enerjisi vardır. Bir orbitalin faz işaretleri (+) ya da (−) olabilir.

2. Atomik orbitaller örtüştüğünde **moleküler orbitalleri (MO'leri)** oluştururlar. Moleküler orbitaller iki (ya da fazla) çekirdeği kapsayan uzayda elektronların bulunabileceği bölgelerdir. Atomik orbitallerde olduğu gibi, moleküler orbitaller de spinleri eşleşmiş iki elektron bulundurabilirler.
3. Aynı faz işaretli atomik orbitaller etkileştiğinde **bir bağlayıcı moleküler orbital** oluşur:



Bir bağlayıcı moleküler orbitalin elektron bulunma yoğunluğu iki çekirdek arasındaki uzay bölgesinde fazladır. Bu bölgedeki negatif elektronlar pozitif çekirdekleri birarada tutarlar.

4. Zıt faz işaretli orbitaller örtüştüğünde bir **karşıtbağlayıcı moleküler orbital** oluşur:



Bir karşıtbağlayıcı orbitalin enerjisi bağlayıcı orbitalinkinden yüksektir. Çekirdekler arasındaki bölgede elektron bulunma yoğunluğu düşüktür ve $\psi = 0$ olan bölgede bir **düğüm** içerir. Bu nedenle, karşıtbağlayıcı orbitallerde elektron bulunması çekirdekleri birarada tutmaz. Çekirdekler arası itme onları birbirinden uzaklaştırır.

5. Bağlayıcı bir moleküler orbitaldeki **elektronların enerjisi** ayrı ayrı atomik orbitallerdeki elektronların enerjisinden düşüktür. Karşıtbağlayıcı bir moleküler orbitaldeki elektronların enerjisi ise ayrı ayrı atomik orbitallerdeki elektronların enerjisinden yüksektir.
6. **Moleküler orbitallerin sayısı** her zaman, bunları oluşturan atomik orbitallerin sayısına eşittir. İki atomik orbitalin biraraya gelmesiyle her zaman, biri bağlayıcı biri de karşıtbağlayıcı olan iki moleküler orbital oluşur.
7. **Melez atomik orbitaller**, farklı türlerde (örneğin *s* ve *p* orbitalleri) ancak aynı atoma ait olan orbitallerin dalga fonksiyonlarının biraraya gelmesi (melezleşmesi) yoluyla elde edilirler.
8. Üç *p* orbitali ile bir *s* orbitalinin melezleşmesi dört **sp^3 orbitali** oluşturur. Bu dört sp^3 orbitalinin eksenleri atomun merkez olduğu düzgün dörtyüzlünün köşelerine yönelmiştir. Metandaki karbon sp^3 melezleşmiştir ve **düzgün dörtyüzlü** yapıdadır.
9. İki *p* orbitali ile bir *s* orbitalinin melezleşmesi üç **sp^2 orbitali** oluşturur. Bu üç sp^2 orbitalinin eksenleri atomun merkez olduğu eşkenar üçgenin köşelerine yönelmiştir. Etendeki karbon atomu sp^2 melezleşmiştir ve **üçgen düzlemsel** yapıdadır.

10. Bir *p* orbitali ile bir *s* orbitalinin melezleşmesi iki ***sp* orbitali** oluşturur. *sp* Melezleşmiş atomlarda bu iki *sp* orbitalinin eksenleri zıt yönlere doğrudur (180°'lik bir açıyla). Etinin karbon atomları *sp* melezleşmiştir ve etin **doğrusal** bir moleküldür.

11. **Sigma bağı** (bir tür birli bağ), bağ ekseni boyunca bakıldığında halkasal simetrik elektron yoğunluğu olan bir bağdır. Genellikle, organik moleküllerin iskeletleri sigma bağıyla bağlı atomlarla oluşturulur.

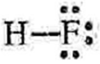
12. İkili ve üçlü bağlardan bir kısmını oluşturan **pi bağı**nda, iki komşu ve paralel *p* orbitalinin elektron yoğunlukları bir bağlayıcı pi moleküler orbitali oluşturmak için yanyana örtüşür.

Problem 1.1 ➤ Aşağıdaki her bir bileşiğin Lewis yapısını yazınız:

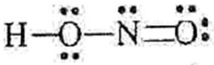
(a) HF (c) CH_3F (e) H_2SO_3 (g) H_3PO_4 (i) HCN

(b) F_2 (d) HNO_2 (f) BH_4^- (h) H_2CO_3

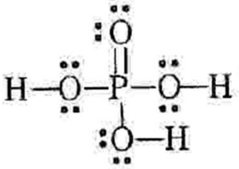
1.1 (a)



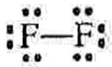
(d)



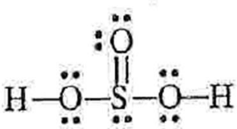
(g)



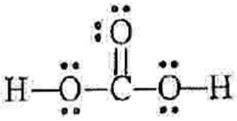
(b)



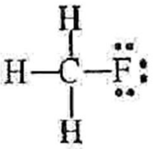
(e)



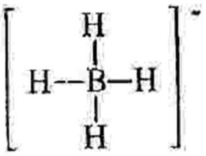
(h)



(c)



(f)



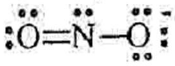
(i) $H-C\equiv N:$

Aşağıdaki negatif iyonların her biri için bir Lewis yapısı yazınız ve formal negatif yükün hangi atomda olduğunu belirtiniz. ◄ **Problem 1.2**

(a) NO_2^- (c) CN^- (e) HCO_3^-

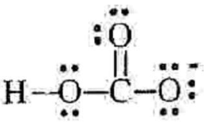
(b) NH_2^- (d) HSO_4^- (f) HC_2^-

1.2 (a)

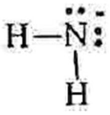


(c) $^{-}:C\equiv N:$

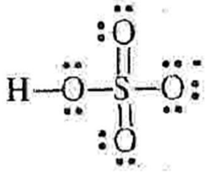
(e)



(b)



(d)

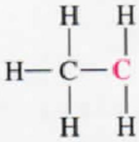


(f) $H-C\equiv C:^{-}$

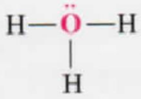
Problem 1.3

Aşağıdaki her bir yapının renkli gösterilen atomunun formal yükünü belirleyiniz:

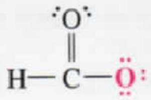
(a)



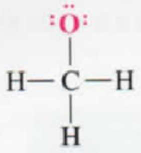
(b)



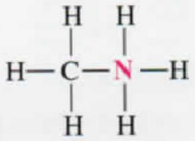
(c)



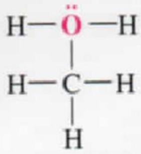
(d)



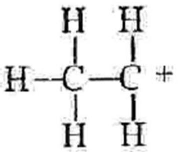
(e)



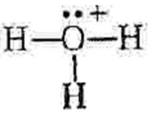
(f)



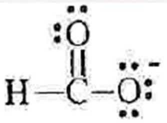
1.3 (a)



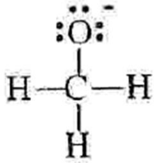
(b)



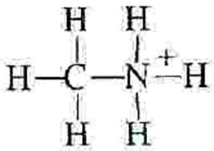
(c)



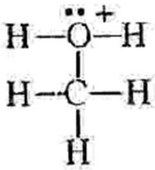
(d)



(e)



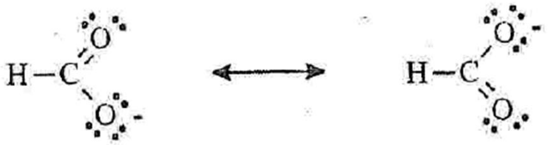
(f)



Problem 1.4

(a) Format iyonu HCO_2^- için iki rezonans yapısı yazınız. (Uyarı: Hidrojen ve oksijen atomları karbona bağlıdır.) **(b)** Format iyonunun karbon-oksijen bağ uzunlukları için bu yapılardan elde edeceğiniz verileri ve **(c)** oksijen atomları üzerindeki yükleri açıklayınız.

1.4 (a)



(b) and (c). Since the two resonance structures are equivalent, each should make an equal contribution to the overall hybrid. The C—O bonds should therefore be of equal length (they should be of bond order 1.5), and each oxygen atom should bear a 0.5 negative charge.

Problem 1.5

(a) Temel halde bir karbon atomunu düşününüz. Böyle bir atom metanın karbonu için yeterli bir model oluşturabilir mi? Değilse neden? (İpucu: Temel halde bir karbon atomunun dört değerlikli olup olamayacağını ve eğer olursa hidrojen atomlarıyla birleşme sonucunda bağ açılarının ne olacağını düşününüz.)

(b) Uyarılmış halde bir karbon atomunu düşününüz:

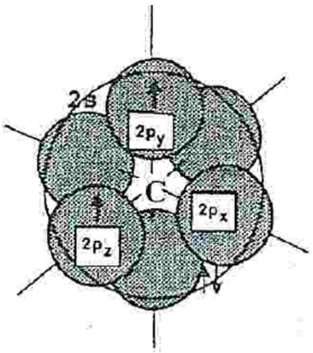
C ⇅ 1 1 1 1

$1s$ $2s$ $2p_x$ $2p_y$ $2p_z$

Bir karbon atomunun uyarılmış hali

Böyle bir atom metandaki karbon için uygun bir model oluşturabilir mi? Değilse neden?

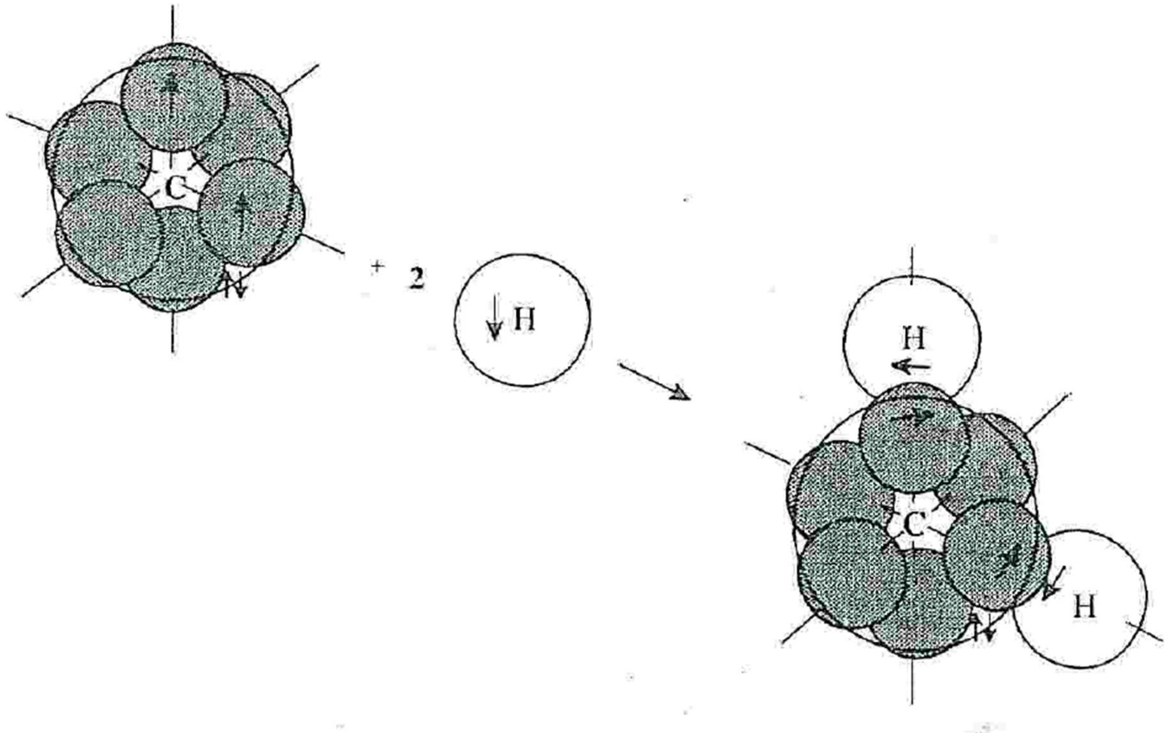
1.5 (a) In its ground state, the valence electrons of carbon might be disposed as shown in the following figure.



The electronic configuration of a ground state carbon atom. The p orbitals are designated $2p_x$, $2p_y$, and $2p_z$ to indicate their respective orientations along the x, y, and z axes. The assignment of the unpaired electrons to the $2p_y$ and $2p_x$ orbitals is arbitrary. They could also have been placed in the $2p_x$ and $2p_z$ or $2p_y$ and $2p_z$ orbitals. (To have placed them both in the same orbital would not have been correct, however, for this would have violated Hund's rule.) (Section 1.10.)

The formation of the covalent bonds of methane *from individual atoms* requires that the carbon atom overlap its orbitals containing *single electrons* with $1s$ orbitals of hydrogen atoms (which also contain a single electron). If a ground state carbon atom were to combine with hydrogen atoms in this way, the result would be that depicted below. *Only two carbon-hydrogen bonds would be formed, and these would be at right angles to each other.*

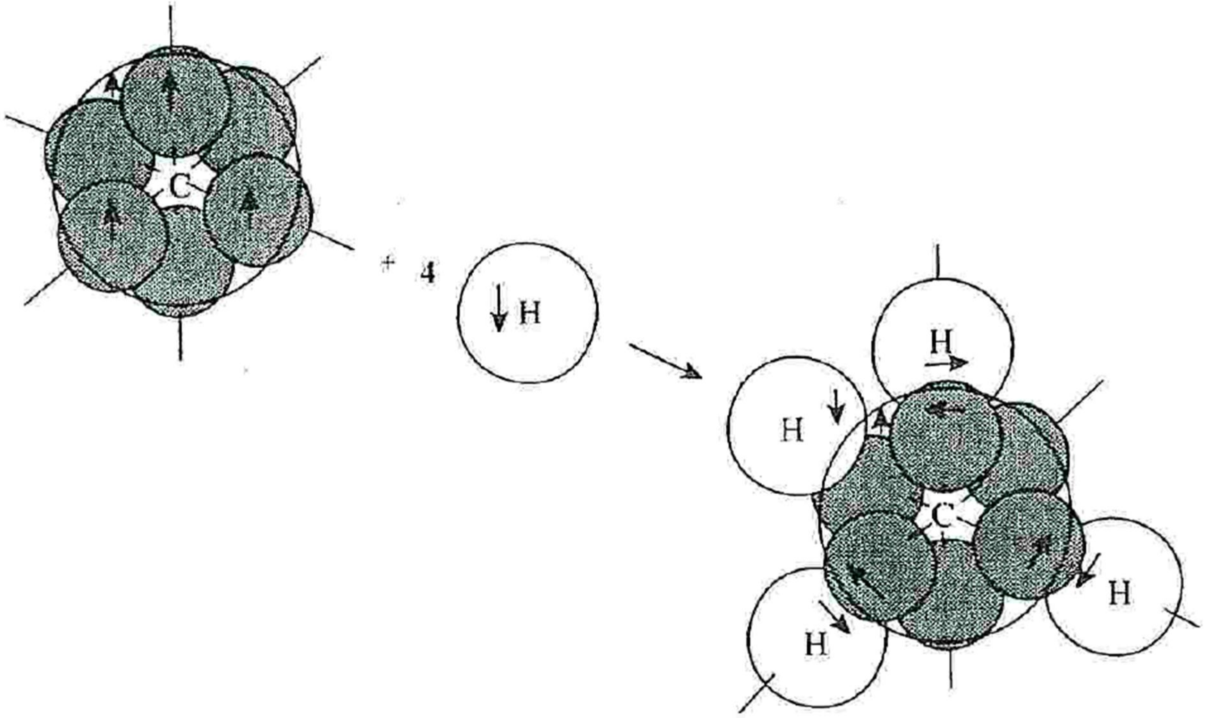
The hypothetical formation of CH_2 from a carbon atom in its ground state.



(b) An excited-state carbon atom might combine with four hydrogen atoms as shown in the figure above.

The promotion of an electron from the $2s$ orbital to the $2p_z$ orbital requires energy. The amount of energy required has been determined and is equal to 400 kJ mol^{-1}. This expenditure of energy can be rationalized by arguing that the energy released when two additional covalent bonds form would more than compensate for that required to excite the electron. No doubt this is true, but it solves only one problem. The problems that cannot be solved by using an excited-state carbon as a basis for a model of methane are the problems of the carbon-hydrogen bond angles and the apparent equivalence of all four carbon-hydrogen bonds. Three of the hydrogens—those overlapping their $1s$ orbitals with the three p orbitals—would, in this model, be at angles of 90° with respect to each other; the fourth hydrogen, the one overlapping its $1s$ orbital with the $2s$ orbital of carbon, would be at some other angle, probably as far from the other bonds as the confines of the molecule would allow. Basing our model of methane on this excited state of carbon gives us a carbon that is tetravalent *but one that is not tetrahedral*, and it predicts a structure for methane in which one carbon-hydrogen bond differs from the other three.

The hypothetical formation of CH_4 from an excited-state carbon atom.



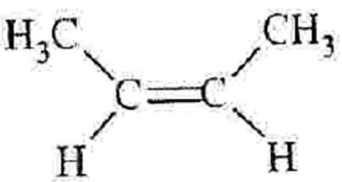
Aşağıdaki alkenlerden hangilerinin cis–trans izomerleri olabilir? Yapılarını yazınız. ◀ **Problem 1.2**

(a) $CH_2{=}CHCH_2CH_3$ (c) $CH_2{=}C(CH_3)_2$

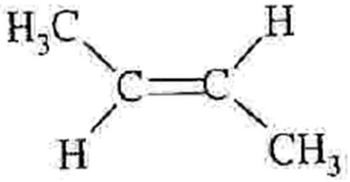
(b) $CH_3CH{=}CHCH_3$ (d) $CH_3CH_2CH{=}CHCl$

1.6 (a) Cis-trans isomers are not possible.

(b)

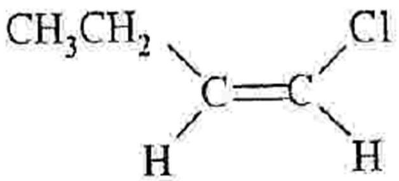


and

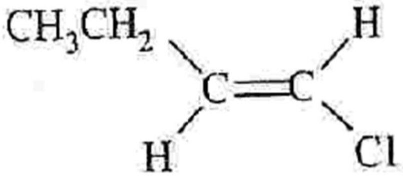


(c) Cis-trans isomers are not possible.

(d)

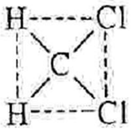


and

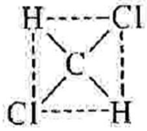


Metan için van't Hoff ve Le Bel'in düzgün dörtyüzlü yapı önermelerinin nedenlerinden biri, sübstitüe metanların mümkün olabilecek izomer sayılarına dayanmaktaydı. Örneğin, CH_2Cl_2 formülünde sadece bir tane bileşik gözlenmiştir (izomerleri yoktur). Kare düzlemsel yapıyı ve düzgün dörtyüzlü yapıyı CH_2Cl_2 için göz önüne alarak bu gözlemin düzgün dörtyüzlü yapıyı nasıl desteklediğini açıklayınız. ◄ **Problem 1.7**

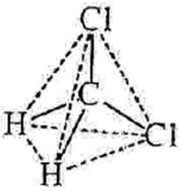
1.7 If the geometry of the carbon atom were square planar, two isomeric compounds with the formula CH_2Cl_2 should exist.



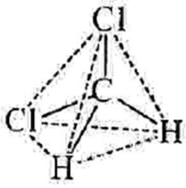
and



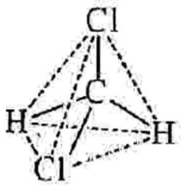
The fact that only one form of CH_2Cl_2 has ever been detected supports a tetrahedral geometry for carbon, because with a tetrahedral geometry only one compound with the formula CH_2Cl_2 is possible. All of the following structures are just different orientations of the same molecule.



is the same as



is the same as



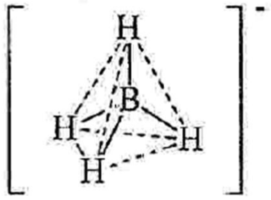
etc.

Make models to convince yourself of this fact.

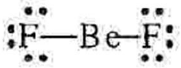
VSEPR kuramını kullanarak aşağıdaki moleküllerin ve iyonların geometrilerini tahmin ediniz: ◄ **Problem 1.8**

(a) BH_4^- **(c)** NH_4^+ **(e)** BH_3 **(g)** SiF_4
(b) BeF_2 **(d)** H_2S **(f)** CF_4 **(h)** $:CCl_3^-$

1.8 (a) There are four bonding pairs. The geometry is tetrahedral.

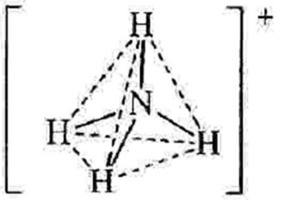


(b) There are two bonding pairs about the central atom. The geometry is linear.

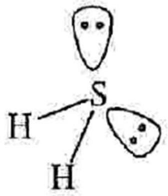


$:\underset{\cdot\cdot}{\ddot{F}}-Be-\underset{\cdot\cdot}{\ddot{F}}:$

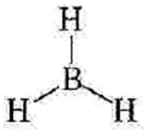
(c) There are four bonding pairs. The geometry is tetrahedral.



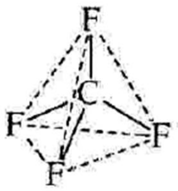
(d) There are two bonding pairs and two nonbonding pairs. The geometry is angular.



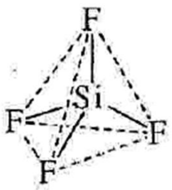
(e) There are three bonding pairs. The geometry is trigonal planar.



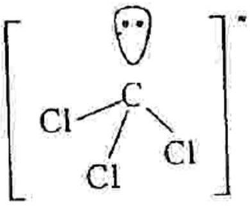
(f) There are four bonding pairs around the central atom. The geometry is tetrahedral.



(g) There are four bonding pairs around the central atom. The geometry is tetrahedral.

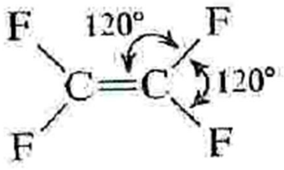


(h) There are three bonding pairs and one nonbonding pair around the central atom. The geometry is trigonal pyramidal.



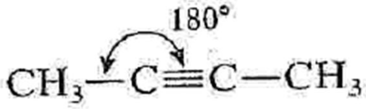
Bağ açılarını tahmin ediniz: **(a)** $F_2C{=}CF_2$ **(b)** $CH_3{\equiv}CCH_3$ **(c)** $HC{\equiv}N$. ◀ **Problem 1.9**

1.9 (a)



, trigonal planar at each carbon atom.

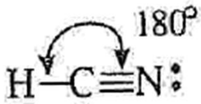
(b)



$$CH_3{-}C{\equiv}C{-}CH_3$$

linear

(c)

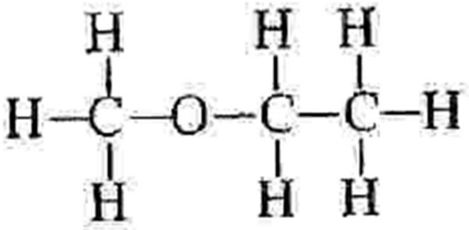


$$H{-}C{\equiv}N\!:$$

linear

Problem 1.10 ➤ Molekül formülü C_3H_8O olan üç yapı izomeri vardır. Bunlardan ikisini propil alkol ve izopropil alkol olarak görmüştük. Üçüncü izomerin çizgili formülünü yazınız.

1.10



Problem 1.11 ➤ Aşağıdaki sıkıştırılmış yapı formüllerinin karbon iskeletlerini belirleyiniz ve her birinin çizgi-bağ formülünü yazınız.

(a) $(CH_3)_2CHCH_2CH_3$

(b) $(CH_3)_2CHCH_2CH_2OH$

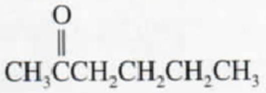
(c) $(CH_3)_2C{=}CHCH_2CH_3$

(d) $CH_3CH_2CH_2CH_2CH_3$

(e) $CH_3CH_2CH(OH)CH_2CH_3$

(f) $CH_2{=}C(CH_2CH_3)_2$

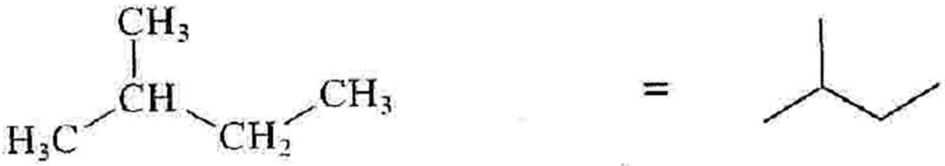
(g)



$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3$

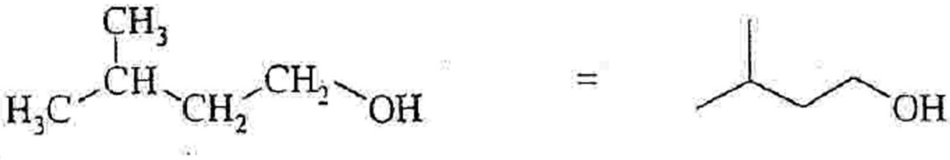
(h) $CH_3CHClCH_2CH(CH_3)_2$

1.11 (a)



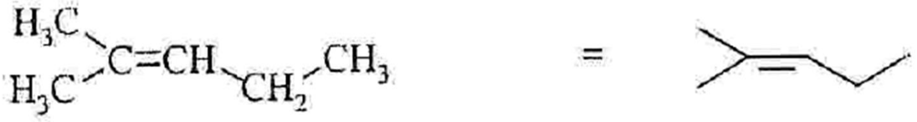
$H_3C-CH(CH_3)-CH_2-CH_3$

(b)



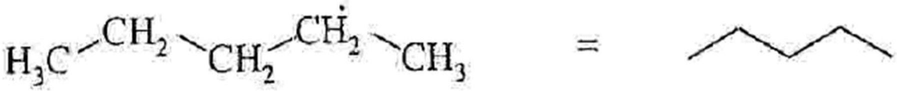
$H_3C-CH(CH_3)-CH_2-CH_2-OH$

(c)



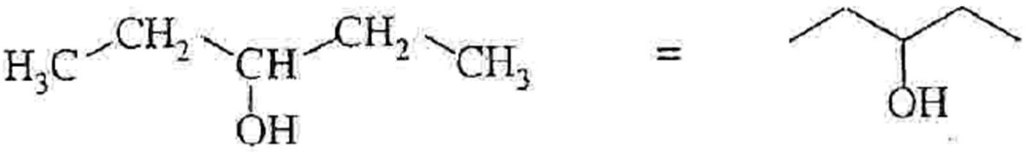
$(H_3C)_2C=CH-CH_2-CH_3$

(d)



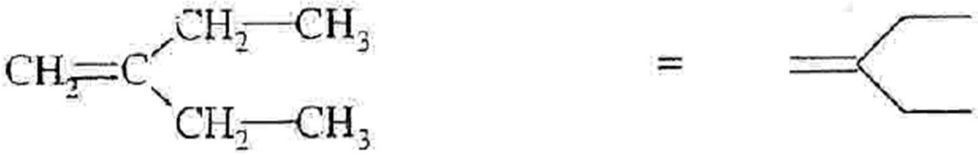
$H_3C-CH_2-CH_2-CH_2-CH_3$

(e)



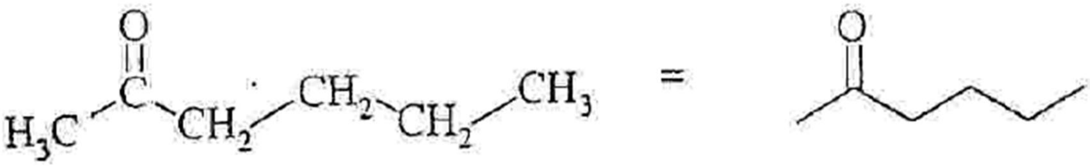
$H_3C-CH_2-CH(OH)-CH_2-CH_3$

(f)



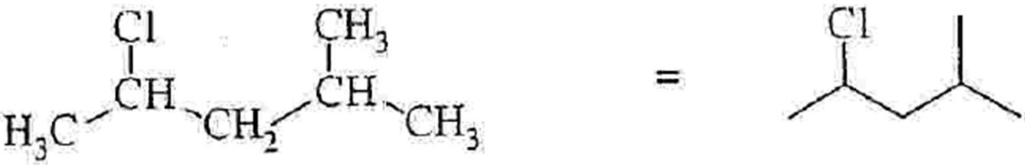
$CH_2=C(CH_2-CH_3)_2$

(g)



$H_3C-C(=O)-CH_2-CH_2-CH_2-CH_3$

(h)



$H_3C-CH(Cl)-CH_2-CH(CH_3)-CH_3$

Problem 1.12 ➤ Problem 1.11'deki hangi moleküllerin yapı izomerleri vardır?

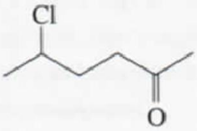
1.12 (a) and (d) are constitutional isomers with the molecular formula C_5H_{12}.

(b) and (e) are constitutional isomers with the molecular formula $C_5H_{12}O$.

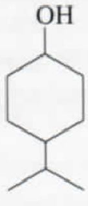
(c) and (f) are constitutional isomers with the molecular formula C_6H_{12}.

Problem 1.13 ➤ Aşağıdaki çizgi-bağ formüllerinin her biri için çizgili formülünü yazınız:

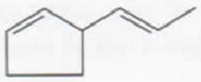
(a)



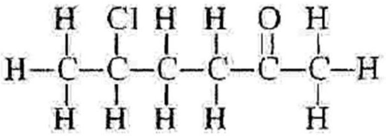
(b)



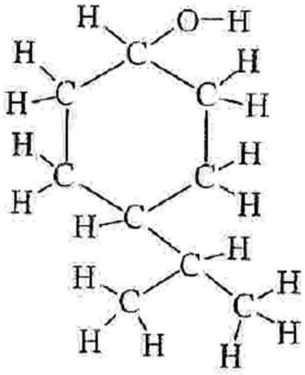
(c)



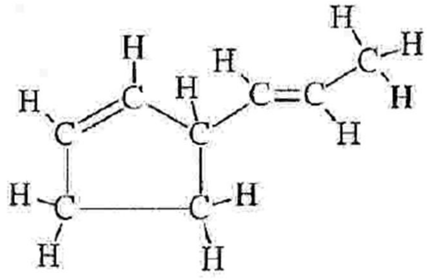
1.13 (a)



(b)

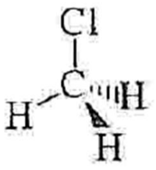


(c)



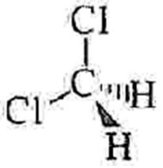
Aşağıdaki bileşiklerden her birini gösteren üç boyutlu (kama-kesikli kama-çizgi) formülleri yazınız: **(a)** CH_3Cl, **(b)** CH_2Cl_2, **(c)** CH_2BrCl **(d)** CH_3CH_2Cl. ◄ **Problem 1.14**

1.14 (a)

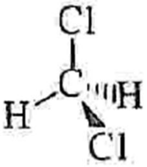


(Note that the **Cl** atom and the three **H** atoms may be written at any of the four positions.)

(b)

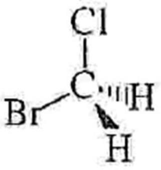


or



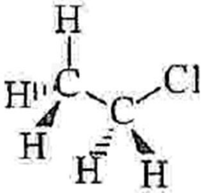
and so on

(c)



and others

(d)



and others

1.15 Aşağıdaki iyonlardan hangileri soygaz elektron dizilişine sahiptir?

(a) Na^+	**(c)** F^+	**(e)** Ca^{2+}	**(g)** O^{2-}
(b) Cl^-	**(d)** H^-	**(f)** S^{2-}	**(h)** Br^+

1.15 (a) Na^+ has the electronic configuration, $1s^22s^22p^6$, of Ne.

(b) Cl^- has the electronic configuration, $1s^22s^22p^63s^23p^6$, of Ar.

(c) F^+ and (h) Br^+ do not have the electronic configuration of a noble gas.

(d) H^- has the electronic configuration, $1s^2$, of He.

(e) Ca^{2+} has the electronic configuration, $1s^22s^22p^63s^23p^6$ of Ar.

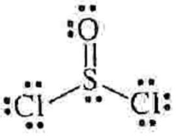
(f) S^{2-} has the electronic configuration, $1s^22s^22p^63s^23p^6$ of Ar.

(g) O^{2-} has the electronic configuration, $1s^22s^22p^6$ of Ne.

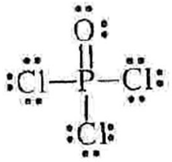
1.16 Aşağıdakilerin Lewis yapılarını yazınız:

(a) $SOCl_2$ **(b)** $POCl_3$ **(c)** PCl_5 **(d)** $HONO_2$ (HNO_3)

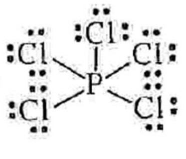
1.16 (a)



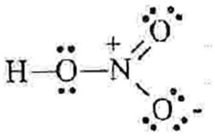
(b)



(c)

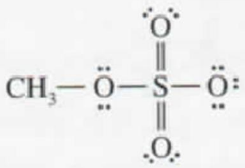


(d)

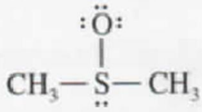


1.17 Aşağıdakilerin her bir atomunun formal yükünü (eğer varsa) belirleyiniz:

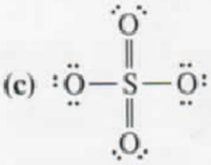
(a)



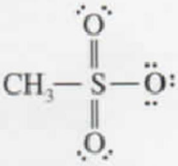
(b)



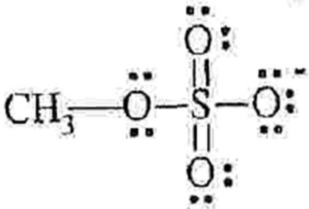
(c)



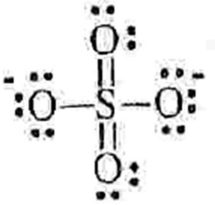
(d)



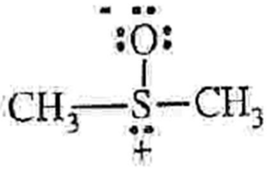
1.17 (a)



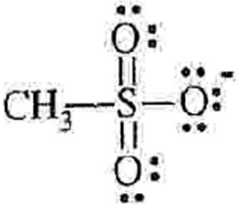
(c)



(b)

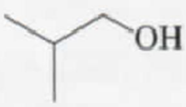


(d)

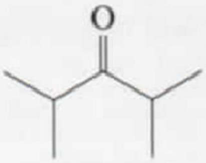


1.18 Verilen her bileşik için çizgisiz bir yapı formülü yazınız.

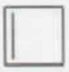
(a)



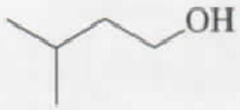
(b)



(c)

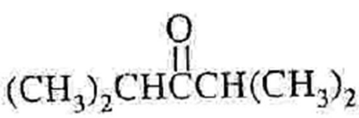


(d)



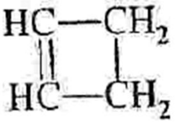
1.18 (a) $(CH_3)_2CHCH_2OH$

(b)



$(CH_3)_2CH\overset{O}{\overset{\|}{C}}CH(CH_3)_2$

(c)



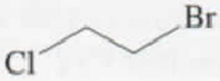
(d) $(CH_3)_2CHCH_2CH_2OH$

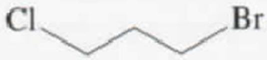
1.19 Problem 1.18'de verilen her bileşiğin molekül formülünü yazınız.

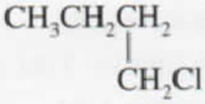
1.19 (a) $C_4H_{10}0$ (c) C_4H_6

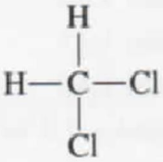
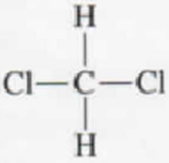
(b) $C_7H_{14}0$ (d) $C_5H_{12}0$

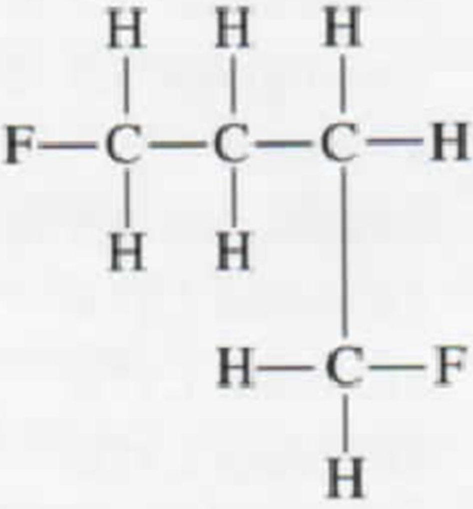
1.20 Aşağıdaki yapı formülleri çiftlerini göz önüne alarak iki formülün aynı bileşiği mi gösterdiğini, ya da yapı izomerleri olan farklı bileşikleri mi temsil ettiklerini, yoksa izomerik olmayan farklı bileşikleri mi gösterdiklerini belirleyiniz.

(a) 

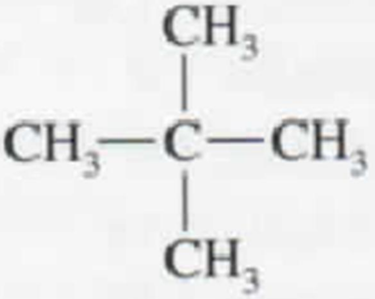
ve 

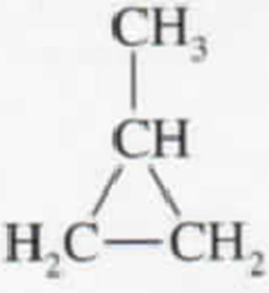
(b) 
$CH_3CH_2CH_2(CH_2Cl)$
ve $ClCH_2CH(CH_3)_2$

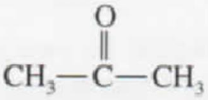
(c) 
$H—CH(Cl)_2$
ve 
$Cl—CH_2—Cl$

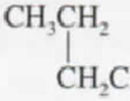
(d) 

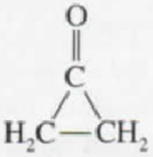
ve $CH_2FCH_2CH_2CH_2F$

(e) 
$CH_3—C(CH_3)_2—CH_3$
ve $(CH_3)_3C—CH_3$

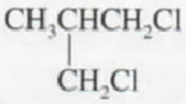
(f) $CH_2{=}CHCH_2CH_3$ ve 

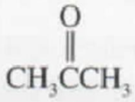
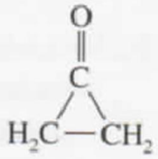
(g) $CH_3OCH_2CH_3$ ve 
$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

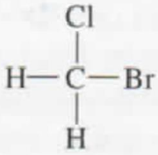
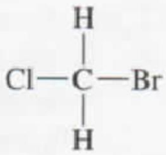
(h) 
$\underset{\displaystyle CH_2CH_3}{\underset{|}{CH_3CH_2}}$ ve $CH_3CH_2CH_2CH_3$

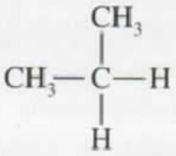
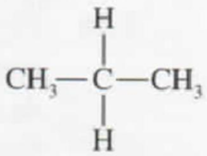
(i) $CH_3OCH_2CH_3$ ve 

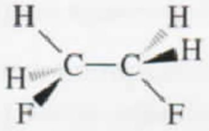
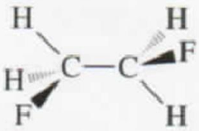
(j) $CH_2ClCHClCH_3$ ve $CH_3CHClCH_2Cl$

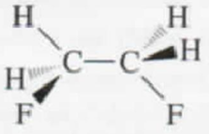
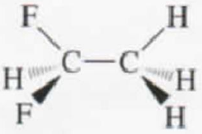
(k) $CH_3CH_2CHClCH_2Cl$ ve 
$CH_3\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}CH_2Cl$

(l) 
$CH_3\overset{O}{\overset{\|}{C}}CH_3$ ve 

(m) 
$H-\overset{Cl}{\overset{|}{\underset{H}{\underset{|}{C}}}}-Br$ ve 
$Cl-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-Br$

(n) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}-H$ ve 
$CH_3-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-CH_3$

(o)  ve 

(p)  ve 

1.20 (a) Different compounds, not isomeric

(b) Constitutional isomers

(c) Same compound

(d) Same compound

(e) Same compound

(f) Constitutional isomers

(g) Different compounds, not isomeric

(h) Same compound

(i) Different compounds, not isomeric

(j) Same compound

(k) Constitutional isomers

(l) Different compounds, not isomeric

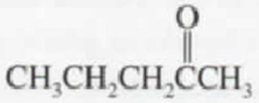
(m) Same compound

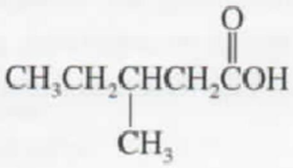
(n) Same compound

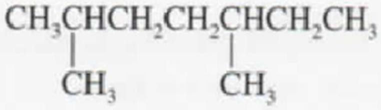
(o) Same compound

(p) Constitutional isomers

1.21 Aşağıdakilerden her birini çizgi-bağ formüllerini kullanarak yeniden yazınız:

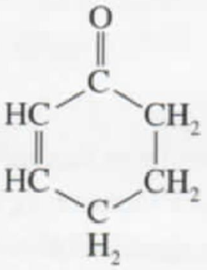
(a) 
$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$

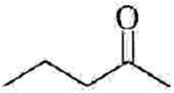
(d) 
$CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}OH$

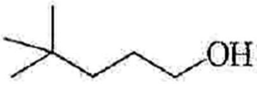
(b) 
$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2\underset{CH_3}{\underset{|}{C}}HCH_2CH_3$

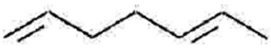
(e) $CH_2{=}CHCH_2CH_2CH{=}CHCH_3$

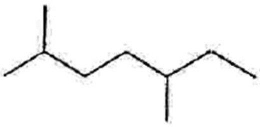
(c) $(CH_3)_3CCH_2CH_2CH_2OH$

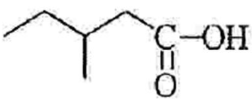
(f) 

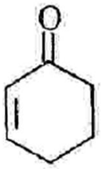
1.21 (a) 

(c) 

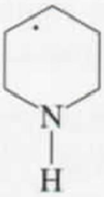
(e) 

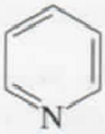
(b) 

(d) 

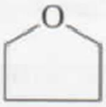
(f) 

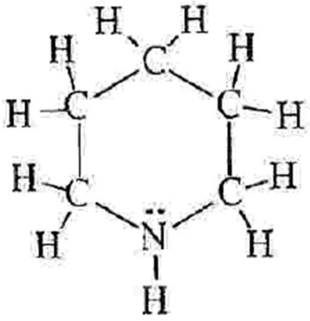
1.22 Aşağıdakilerin her biri için ortaklaşılmamış elektron çiftlerini gösteren bir çizgili formül yazınız:

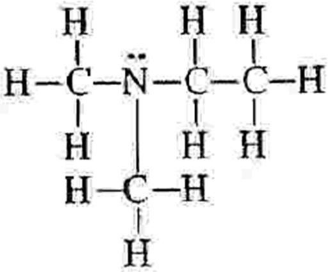
(a) 

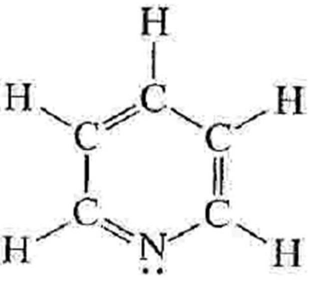
(b) 

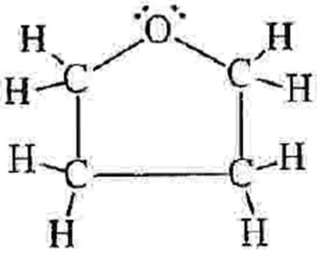
(c) $(CH_3)_2NCH_2CH_3$

(d) 

1.22 (a) 

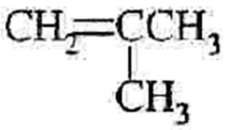
(c) 

(b) 

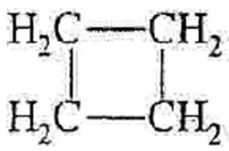
(d) 

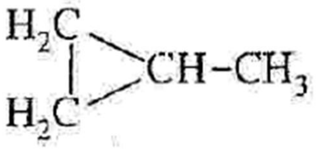
1.23 Molekül formülü C_4H_8 olan bütün yapı izomerleri için yapı formüllerini istediğiniz şekilde yazınız.

1.23 $CH_2{=}CHCH_2CH_3$ $CH_3CH{=}CHCH_3$



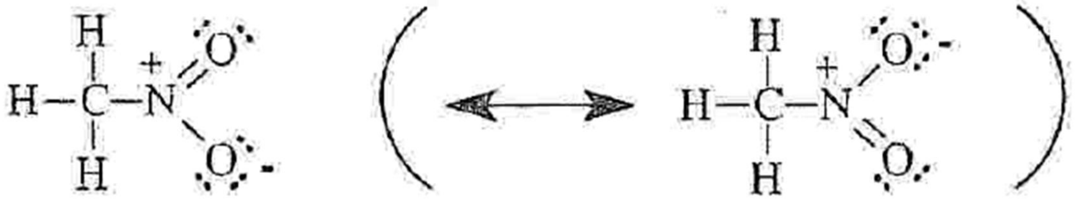
$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_3$

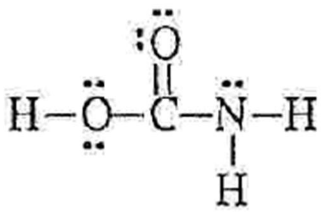


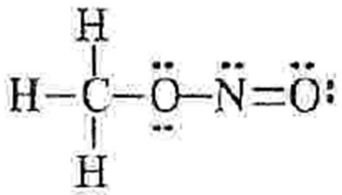


1.24 Molekül formülü CH_3NO_2 olan bileşiğin en az üç yapı izomerinin yapı formüllerini yazınız. (Bu soruyu cevaplandırırken formal yük taşıyan atomların bu yüklerini belirtmelisiniz.)

1.24







(Other structures are possible.)

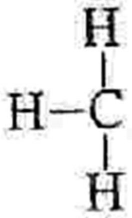
***1.25** Siyanik asit (H—O—C≡N) ve izosiyanik asit (H—N=C=O), elektronları farklı yerlerde bulunan, ancak yapıları rezonans yapıları temsil etmeyen bileşiklerdir. **(a)** Açıklayınız. **(b)** Siyanik asitten proton kaybı, izosiyanik asitten proton kaybıyla aynı anyonu oluşturur. Açıklayınız.

1.25 (a) While the structures differ in the position of their electrons, they also differ in the positions of their nuclei and thus *they are not resonance structures.* (In cyanic acid the hydrogen nucleus is bonded to oxygen; in isocyanic acid it is bonded to nitrogen.)

(b) The anion obtained from either acid is a resonance hybrid of the following structures: $^{-}:\ddot{\underset{\cdot\cdot}{O}}{-}C{\equiv}N:$ $\longleftrightarrow$ $:\ddot{O}{=}C{=}\ddot{N}:^{-}$

1.26 Bir karbon atomunun üç hidrojen atomuna birli bağla bağlı olduğu ve karbon atomunun başka değerlik elektronunun bulunmadığı kimyasal yapıları (molekül ya da iyon) düşününüz. **(a)** Karbon atomunun formal yükü ne olur? **(b)** Yapının toplam yükü ne kadardır? **(c)** Bu yapının şekli nasıldır? **(d)** Karbon atomunun melezleşmesinin nasıl olmasını beklersiniz?

1.26

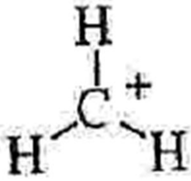


$$\mathrm{H{-}\overset{\overset{\large H}{|}}{\underset{\underset{\large H}{|}}{C}}}$$

(a) A + charge. ($F = 4 - 6/2 = +1$)

(b) A + charge. (It is called a methyl cation.)

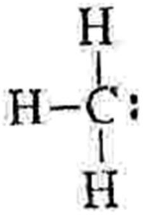
(c) Trigonal planar, that is,



(d) sp^2

1.27 Bir önceki problemdeki gibi karbon atomunun üç hidrojen atomuna birli bağla bağlı olduğu, ancak karbon atomunun ortaklaşılmamış elektron çifti içerdiği bir yapıyı gözönüne alınız. **(a)** Karbon atomunun formal yükü ne olur? **(b)** Yapının toplam yükü ne kadardır? **(c)** Bu yapının şekli nasıldır? **(d)** Karbon atomunun melezleşmesinin nasıl olmasını beklersiniz?

1.27

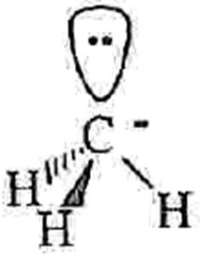


$$H-\overset{H}{\underset{H}{C}}:$$

(a) A − charge. ($F = 4 - 6/2 - 2 = -1$)

(b) A − charge. (It is called a methyl anion.)

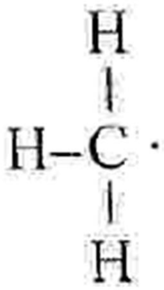
(c) Trigonal pyramidal, that is



(d) sp^3

1.28 Önceki problemlerdeki gibi karbon atomunun üç hidrojen atomuna birli bağla bağlı olduğu, ancak karbon atomunun eşleşmemiş bir elektronunun bulunduğu bir yapıyı gözönüne alınız. **(a)** Karbon atomunun formal yükü ne olur? **(b)** Yapının toplam yükü ne kadardır? **(c)** Bu yapının şekli üçgen düzlemsel olduğuna göre karbon atomunun melezleşmesinin nasıl olmasını beklersiniz?

1.28

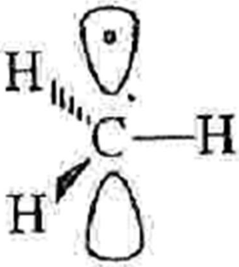


$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\,\cdot}$$

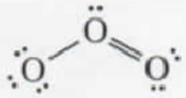
(a) No formal charge. ($F = 4 - 6/2 - 1 = 0$)

(b) No charge.

(c) sp^2, that is,

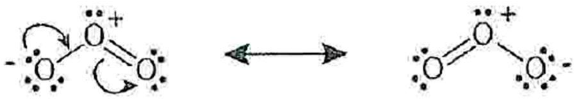


1.29 Ozon (O_3) atmosferin üst tabakalarında bulunur ve orada yüksek enerjili ultraviyole (UV) ışınlarını soğurarak yeryüzünü koruyucu bir ekran görevi görür (bkz. Altbölüm 10.11E). Ozonun olası bir rezonans yapısı aşağıdadır:



(**a**) Bu yapıdaki atomların formal yüklerini belirleyiniz. (**b**) Ozon için eşdeğer bir rezonans yapısı daha yazınız. (**c**) Bu rezonans yapılarına göre, ozonun iki oksijen-oksijen bağının uzunluklarının nasıl olacağını beklersiniz? (**d**) Yukarıdaki yapı ve sizin yazdığınız yapı ozon molekülü için açılı bir şekil öngörmektedir. Bu şekil VSEPR kuramıyla uyumlu mudur? Cevabınızı açıklayınız.

1.29 (a) and (b)

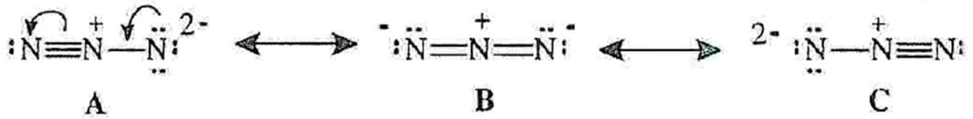


(c) Because the two resonance structures are equivalent, they should make equal contributions to the hybrid and, therefore, the bonds should be the same length.

(d) Yes. We consider the central atom to have two groups or units of bonding electrons and one unshared pair.

1.30 **Azür (N_3^-), iyonunun rezonans yapılarını yazınız. Bu rezonans yapılarının azür iyonundaki bağların aynı uzunlukta olduğunu nasıl gösterdiğini açıklayınız.**

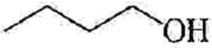
1.30

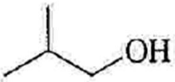


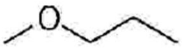
Structures **A** and **C** are equivalent and, therefore, make equal contributions to the hybrid. The bonds of the hybrid, therefore, have the same length.

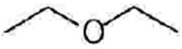
1.31 **Belirtilen türlerdeki yapı formüllerini yazınız: (a) Formülü $C_4H_{10}O$ olan yedi yapı izomeri için çizgi-bağ formülleri. (b) Formülü C_2H_7N olan iki yapı izomeri için sıkıştırılmış yapı formülleri. (c) Formülü C_3H_9N olan iki yapı izomeri için sıkıştırılmış yapı formülleri. (d) Formülü C_5H_{12} olan yedi yapı izomeri için çizgi-bağ formülleri.**

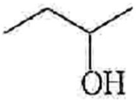
***1.31** (a)

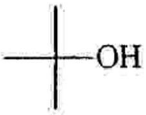


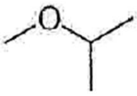






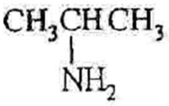






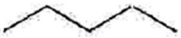
(b) $(CH_3)_2NH$ $CH_3CH_2NH_2$

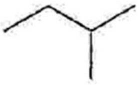
(c) $(CH_3)_3N$ $CH_3CH_2NHCH_3$ $CH_3CH_2CH_2NH_2$

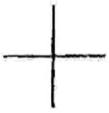


$CH_3\underset{NH_2}{\underset{|}{C}}HCH_3$

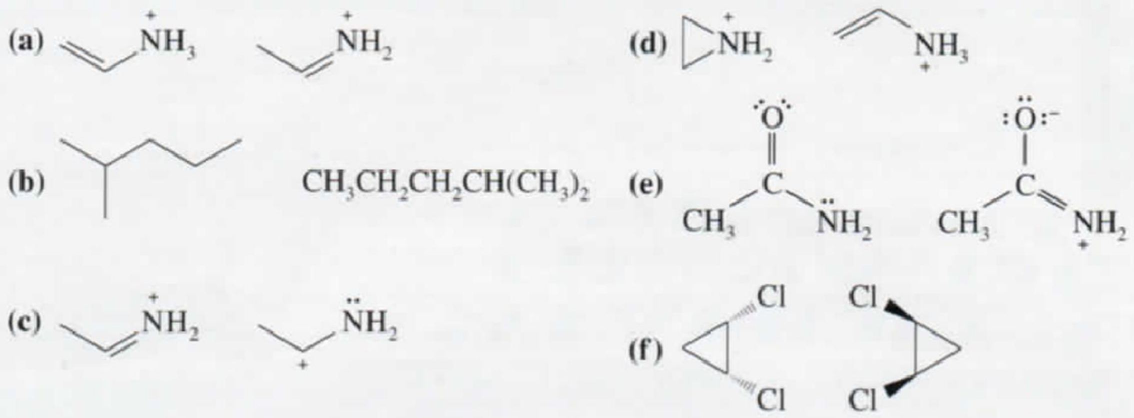
(d)







***1.32** Aşağıdaki çiftler arasındaki ilişki nedir? Yani bunlar yapı izomerleri midir, aynı bileşikler midir ya da başka bir şey midir?



***1.32** (a) constitutional isomers (b) the same
(c) resonance forms (d) constitutional isomers
(e) resonance forms (f) the same

***1.33** Bölüm 15'te derişik nitrik ve sülfürik asit karıştırıldığında nitronyum iyonunun (NO_2^+) nasıl oluştuğunu göreceğiz. **(a)** Nitronyum iyonu için bir Lewis yapısı yazınız. **(b)** VSEPR kuramı NO_2^+ iyonu için hangi geometriyi öngörür? **(c)** NO_2^+ ile aynı sayıda elektron içeren bir yapı yazınız.

***1.33** (a) $:\ddot{O}=\overset{+}{N}=\ddot{O}:$

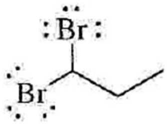
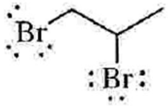
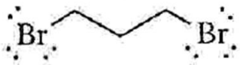
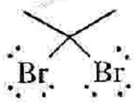
(b) Linear

(c) Carbon dioxide

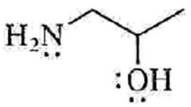
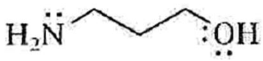
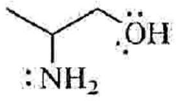
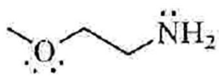
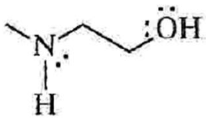
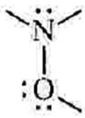
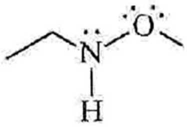
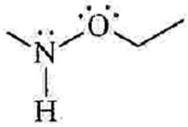
***1.34** Aşağıda verilen atom gruplarından oluşabilecek olası yapı izomerlerinin ya da iyonların çizgi-bağ formüllerini yazınız. Bütün ortaklaşılmamış elektron çiftlerini ve varsa formal yükleri gösteriniz.

Grup	C atomları	H atomları	Diğerleri
A	3	6	2 Br atomu
B	3	9	1 N atomu ve 1 O atomu (aynı C'da değil)
C	3	4	1 O atomu
D	2	7	1 N atomu ve 1 proton
E	3	7	1 fazla elektron

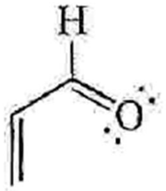
*1.34 Set A:

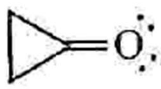





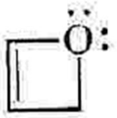
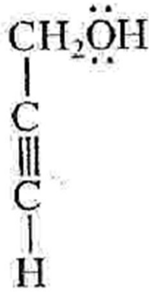
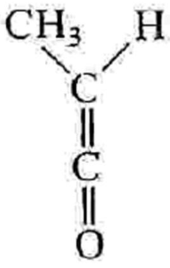
Set B:

Set C:

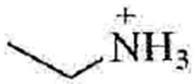
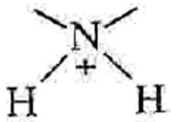

a


b

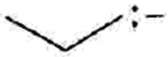
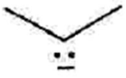



c

[and unstable enol forms of a, b, and c]

Set D:

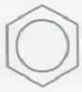
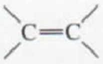
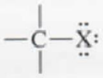
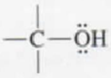
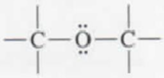
Set E:

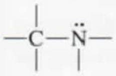
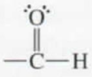
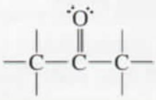
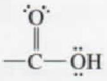
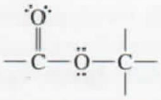
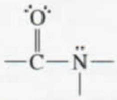
(i.e., $CH_3CH_2\ddot{C}H_2^{-}$ and $CH_3\overset{-}{\ddot{C}}HCH_3$)

Tipik Karbon Bileşikleri: Fonksiyonel Gruplar Moleküller Arası Kuvvetler ve İnfrared (İR) Spektroskopisi

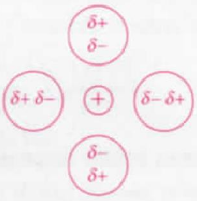
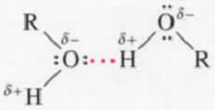
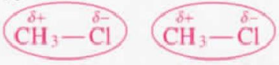
Çizelge 2.3 **Organik Bileşiklerin Önemli Sınıfları**

	Sınıf						
	Alkan	**Alken**	**Alkin**	**Aromatik**	**Haloalkan**	**Alkol**	**Eter**
Özel örnek	CH_3CH_3	$CH_2=CH_2$	$HC\equiv CH$		CH_3CH_2Cl	CH_3CH_2OH	CH_3OCH_3
IUPAC adı	Etan	Eten	Etin	Benzen	Kloroetan	Etanol	Metoksimetan
Yaygın adı[a]	Etan	Etilen	Asetilen	Benzen	Etil klorür	Etil alkol	Dimetil eter
Genel formülü	RH	$RCH=CH_2$ $RCH=CHR$ $R_2C=CHR$ $R_2C=CR_2$	$RC\equiv CH$ $RC\equiv CR$	ArH	RX	ROH	ROR
Fonksiyonel grubu	C—H ve C—C bağları		$-C\equiv C-$	Aromatik halka			

[a] Bu adlar IUPAC tarafından da kabul edilmiştir.

Sınıf						
Amin	**Aldehit**	**Keton**	**Karboksilik Asit**	**Ester**	**Amit**	**Nitril**
CH_3NH_2	$CH_3\overset{\overset{O}{\|}}{C}H$	$CH_3\overset{\overset{O}{\|}}{C}CH_3$	$CH_3\overset{\overset{O}{\|}}{C}OH$	$CH_3\overset{\overset{O}{\|}}{C}OCH_3$	$CH_3\overset{\overset{O}{\|}}{C}NH_2$	$CH_3C\equiv N$
Metanamin	Etanal	Propanon	Etanoik asit	Metil etanoat	Etanamit	Etannitril
Metilamin	Asetaldehit	Aseton	Asetik asit	Metil asetat	Asetamit	Asetonitril
RNH_2 R_2NH R_3N	$R\overset{\overset{O}{\|}}{C}H$	$R\overset{\overset{O}{\|}}{C}R'$	$R\overset{\overset{O}{\|}}{C}OH$	$R\overset{\overset{O}{\|}}{C}OR'$	$R\overset{\overset{O}{\|}}{C}NH_2$ $R\overset{\overset{O}{\|}}{C}NHR'$ $R\overset{\overset{O}{\|}}{C}NR'R''$	RCN
						$-C\equiv N\colon$

Çizelge 2.6 Çekici Elektrik Kuvvetleri

Elektrik Kuvveti	Bağıl Kuvveti	Türü	Örnek
Katyon–anyon (bir kristalde)	Çok kuvvetli	⊕ ⊖	Lityum florür kristal örgüsü
Kovalent bağlar	Kuvvetli (140–435 kJ mol^{-1})	Ortaklaşılmış elektron çiftleri	H — H (435 kJ mol^{-1}) CH_3 — CH_3 (370 kJ mol^{-1}) I — I (150 kJ mol^{-1})
İyon–dipol	Orta		Suda Na^+ (bkz. Şekil 2.9)
Dipol–dipol (hidrojen bağları dahil)	Ortayla zayıf arası (4–38 kJ mol^{-1})	$-\overset{\delta-}{\ddot{Z}}\cdots\overset{\delta+}{H}-$	 ve 
van der Waals	Değişken	Geçici dipol	Metan molekülleri arasındaki etkileşmeler

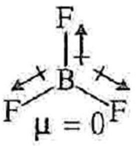
Problem 2.1 ➤ Aşağıdaki moleküllerin her biri için (eğer varsa) dipol momentin yönünü belirtiniz: (a) HF, (b)IBr, (c) Br_2, (d)F_2

2.1 (a) $\underset{+\!\!\!\longrightarrow}{\mathrm{H{-}F}}$ or $\overset{\delta+}{\mathrm{H}}{-}\overset{\delta-}{\mathrm{F}}$ (c) $\mathrm{Br{-}Br}$ $\mu = 0$

(b) $\underset{+\!\!\!\longrightarrow}{\mathrm{I{-}Br}}$ or $\overset{\delta+}{\mathrm{I}}{-}\overset{\delta-}{\mathrm{Br}}$ (d) $\mathrm{F{-}F}$ $\mu = 0$

Bor triflorürün (BF_3) dipol momenti yoktur (μ = 0). BF_3'ün VSEPR kuramıyla öngörülen geometrisinin, bu sonuçla nasıl doğrulandığını açıklayınız. ◄ **Problem 2.2**

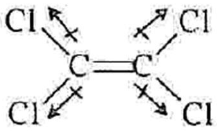
2.2 VSEPR theory predicts a planar structure for BF_3.



The vector sum of the bond moments of a trigonal planar structure would be zero, resulting in a prediction of $\mu = 0$ for BF_3. This correlates with the experimental observation and confirms the prediction of VSEPR theory.

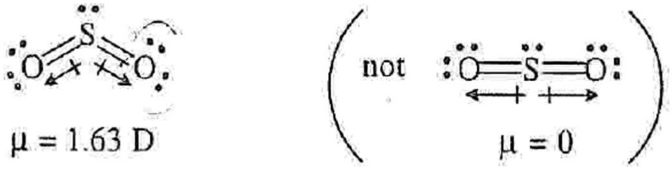
Tetrakloraetenin ($CCl_2{=}CCl_2$) dipol momenti yoktur. $CCl_2{=}CCl_2$'nin şeklini göz önüne alarak bunu açıklayınız. ◄ **Problem 2.3**

2.3 The shape of $CCl_2{=}CCl_2$ (below) is such that the vector sum of all of the C—Cl bond moments is zero.



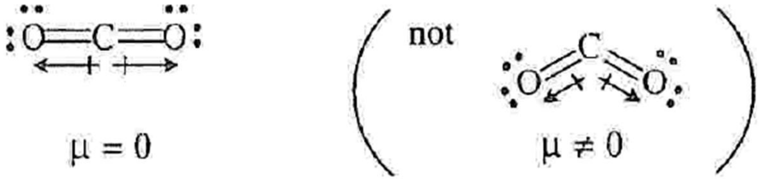
Problem 2.4 ➤ Kükürt dioksitin (SO_2) dipol momenti (μ = 1,63 D) olduğu halde karbon dioksitin (CO_2) dipol momenti (μ = 0) yoktur. Bu sonuçlar, bu iki molekülün geometrileri hakkında ne ifade eder?

2.4 The fact that SO_2 has a dipole moment indicates that the molecule is angular, not linear.



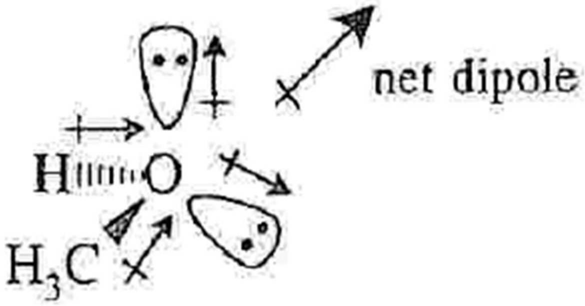
An angular shape is what we would expect from VSEPR theory, too.

The fact that CO_2 has no dipole moment indicates that its shape is linear, not angular.



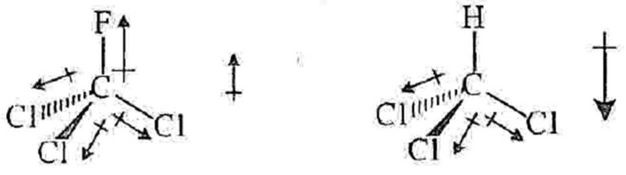
Problem 2.5 ➤ Üç boyutlu bir formül kullanarak, CH_3OH'ün dipol momentinin yönünü gösteriniz.

2.5 Again, this is what VSEPR theory predicts.



Problem 2.6 ➤ Triklorometanın ($CHCl_3$, *kloroform* da denir) $CFCl_3$'ten daha büyük bir dipol momenti vardır. Üç boyutlu yapılarını ve bağ momentlerini kullanarak bu sonucu açıklayınız.

2.6 In $CFCl_3$ the large C—F bond moment opposes the C—Cl moments, leading to a net dipole moment in the direction of the fluorine. Because hydrogen is much less electronegative than fluorine no such opposing effect occurs in $CHCl_3$; therefore, it has a net dipole moment that is larger and in the direction of the chlorine atoms.

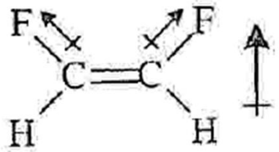


Smaller net dipole moment   Larger net dipole moment

Problem 2.5 ➤ Aşağıdaki bileşiklerin her birinde önemli bağ momentlerinin yönünü belirtiniz (C—H bağlarını ihmal ediniz). Molekül için net dipol momentin yönünü de belirtmelisiniz. Eğer net dipol moment yoksa $\mu = 0$ olarak yazınız.

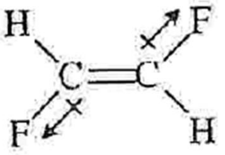
(a) *cis*-CHF = CHF **(c)** $CH_2{=}CF_2$
(b) *trans*-CHF = CHF **(d)** $CF_2{=}CF_2$

2.7 (a)



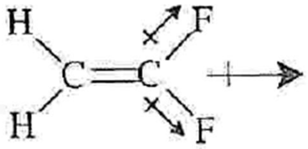
net dipole moment

(b)



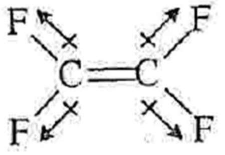
$\mu = 0$

(c)



net dipole moment

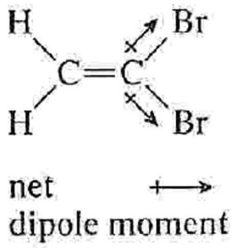
(d)

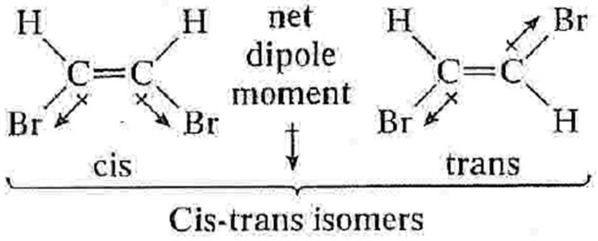


$\mu = 0$

Problem 2.6 ➤ Aşağıdaki alkenlerin hepsi için yapı formüllerini yazınız. (a) formülü $C_2H_2Br_2$ olan ve (b) formülü $C_2Br_2Cl_2$ olan. Her bir durumda bileşikleri cis-trans izomerler olarak belirtiniz. Her birinin dipol momentini tahmin ediniz.

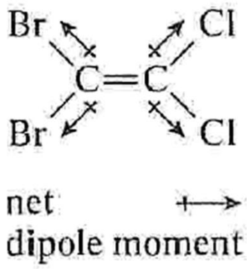
2.8 (a)

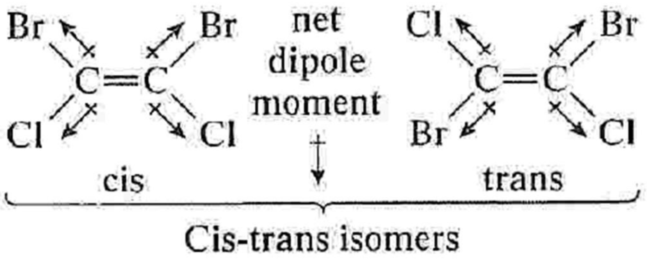




$\mu = 0$

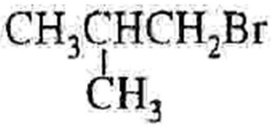
(b)



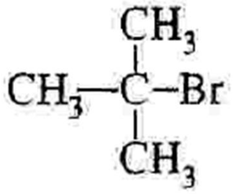


$\mu = 0$

(a) C_4H_9Br formülündeki yapı izomeri olan birincil iki alkil bromür için (b) ikincil bir alkil bromür için ve (c) aynı formüldeki üçüncül bir alkil bromür için yapı formüllerini yazınız. ◄ **Problem 2.5**

2.9 (a) $CH_3CH_2CH_2CH_2Br$ and  $CH_3\underset{CH_3}{CH}CH_2Br$

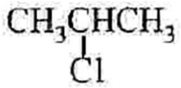
(b) $CH_3\underset{Br}{CH}CH_2CH_3$

(c)  $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br$

Problem 2.6

Organik bileşiklerin adlandırılmasını ileride her bir sınıfı ayrıntılı olarak gördüğümüzde inceleyecek olmamıza karşın, alkil halojenürlerin adlandırılmasında kullanılan bir yöntem burada açıklayacağımız kadar basittir. Halojene bağlı alkil grubunu basit olarak adlandırıp sonuna *florür*, *klorür*, *bromür* ya da *iyodür* kelimesini ekleriz. (a) Etil florür ve (b) izopropil klorürün formüllerini yazınız. (c) $CH_3CH_2CH_2Br$, (d) CH_3CHFCH_3 ve (e) C_6H_5I'nın adları nedir?

2.10 (a) CH_3CH_2F

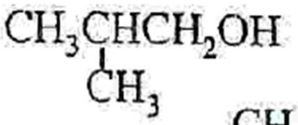
(b)  $CH_3\underset{Cl}{CH}CH_3$ or $(CH_3)_2CHCl$

(c) Propyl bromide

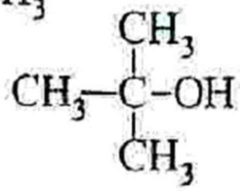
(d) Isopropyl fluoride

(e) Phenyl iodide

Problem 2.11 $C_3H_{10}O$ formülüne sahip (a) iki birincil alkol (b) bir ikincil alkol ve (c) bir üçüncül alkol için yapı formüllerini yazınız.

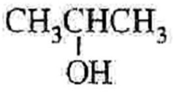
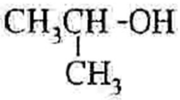
2.11 (a) $CH_3CH_2CH_2CH_2OH$ and  $CH_3\underset{CH_3}{CH}CH_2OH$

(b) $CH_3\underset{OH}{CH}CH_2CH_3$

(c)  $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$

Problem 2.12 Alkolleri adlandırmanın bir yolu da —OH grubuna bağlı alkil grubunu adlandırmak ve sonra *alkol* kelimesini eklemektir. (a) Propil alkol ve (b) izopropil alkolün yapılarını yazınız.

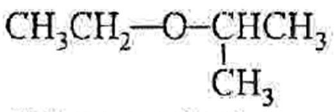
2.12 (a) $CH_3CH_2CH_2OH$

(b)  $CH_3\underset{OH}{CH}CH_3$ or  $CH_3\underset{CH_3}{CH}-OH$

Problem 2.13

Eterleri adlandırmanın bir yolu, oksijene bağlı alkil gruplarının adlarının alfabetik olarak sıralanması ve sonuna *eter* kelimesinin eklenmesidir. Örneğin, *dimetil eter*de olduğu gibi iki alkil grubu da aynıysa *di-* ön ekini kullanırız. (a) dietil eter (b) etil propil eter ve (c) etil izopropil eter için yapı formüllerini yazınız. (d) $CH_3OCH_2CH_2CH_3$ (e) $(CH_3)_2CHOCH(CH_3)_2$ ve (f) $CH_3OC_6H_5$ formülündeki eterlere hangi adları verirsiniz?

2.13 (a) $CH_3CH_2{-}O{-}CH_2CH_3$ (b) $CH_3CH_2{-}O{-}CH_2CH_2CH_3$

(c) 

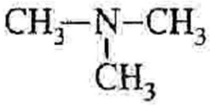
$CH_3CH_2{-}O{-}\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$

(d) Methyl propyl ether

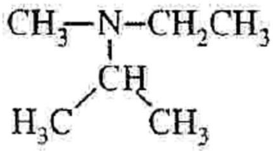
(e) Diisopropyl ether (f) Methyl phenyl ether

Problem 2.14 ➤ Aminleri adlandırmanın bir yolu, azota bağlı alkil gruplarının alfabetik olarak sıralanması, eğer gruplar aynıysa *di-* ve *tri-* ön eklerinin kullanılmasıdır. $(CH_3)_2CHNH_2$ için *izopropilamin* adı bu adlandırmaya bir örnektir. (a) propilamin, (b) trimetilamin ve (c) etilizopropilmetilaminin formüllerini yazınız. (d) $CH_3CH_2CH_2NHCH(CH_3)_2$ (e) $(CH_3CH_2CH_2)_3N$ ve (f) $C_6H_5N(CH_3)_2$'nin adı nedir?

2.14 (a) $CH_3CH_2CH_2NH_2$

(b) 

$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{N}}{-}CH_3$ or $(CH_3)_3N$

(c) 

(d) Isopropylpropylamine

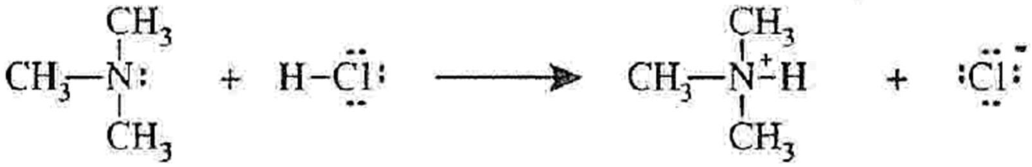
(e) Tripropylamine (f) Methylphenylamine

(g) Dimethylphenylamine

Problem 2.15 ➤ Problem 2.14'teki aminlerden hangisi (a) birincil amin (b) ikincil amin ve (c) üçüncül amindir?

2.15 (a) (a) only (b) (d,f) (c) (b, c, e, g)

Problem 2.16 ➤ Aminler zayıf baz olarak amonyağa benzerler. Bunu, ortaklaşılmamış elektron çiftlerini proton alımında kullanarak gerçekleştirirler. (a) Trimetilaminle HCl arasında gerçekleşecek tepkimeyi gösteriniz. (b) Bu tepkime ürünündeki azot atomu için hangi melezleşme halini öngörürsünüz?

2.16 (a) 

$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\ddot{N}}}: + H{-}\ddot{\underset{..}{Cl}}: \longrightarrow CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{+}{N}}}{-}H + :\ddot{\underset{..}{Cl}}:^-$$

(b) *sp*^{3}

Problem 2.17 ➤ Aşağıdaki her bir bileşik çifti aynı (ya da benzer) molekül kütlesine sahiptir. Her bir çiftteki hangi bileşiğin kaynama noktasının daha yüksek olmasını beklersiniz? Cevaplarınızı açıklayınız. (a)$CH_3CH_2CH_2CH_2OH$ veya $CH_3CH_2OCH_2CH_3$, (b) $(CH_3)_3N$ veya $CH_3CH_2NHCH_3$, (c) $CH_3CH_2CH_2CH_2OH$ veya $HOCH_2CH_2CH_2OH$.

2.17 (a) $CH_3CH_2CH_2CH_2OH$ would boil higher because its molecules can form hydrogen bonds to each other through the $-\ddot{\underset{\cdot\cdot}{O}}-H$ group.

(b) $CH_3CH_2NHCH_3$ would boil higher because its molecules can form hydrogen bonds to each other through the $-\underset{|}{\ddot{N}}-H$ group.

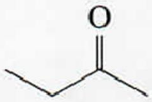
(c) $HOCH_2CH_2CH_2OH$ because by having two $-\ddot{\underset{\cdot\cdot}{O}}-H$ groups, it can form more hydrogen bonds.

Problem 2.18 ➤ Propan ya da siklopropandan hangisinin erime noktasının daha yüksek olacağını beklersiniz? Cevabınızı açıklayınız.

2.18 Cyclopropane would have the higher melting point because its cyclic structure gives it a rigid compact shape that would permit stronger crystal lattice forces.

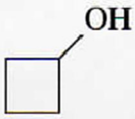
2.19 Aşağıdaki bileşiklerden her birini bir alkan, alken, alkin, alkol, aldehit, amin vb. olarak sınıflandırınız

(a)

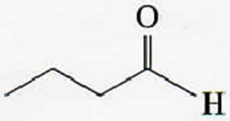


(b) $CH_3-C\equiv CH$

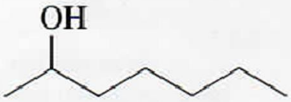
(c)



(d)

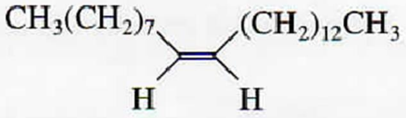


(e)



(karanfil yağından elde edilir)

(f)



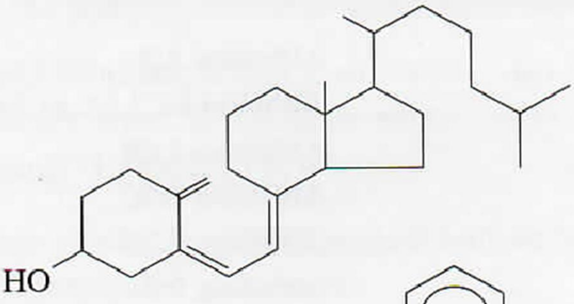
(karasineğin cinsel çekicisi)

2.19 (a) Ketone (b) Alkyne (c) Alcohol (d) Aldehyde

(e) Alcohol (f) Alkene

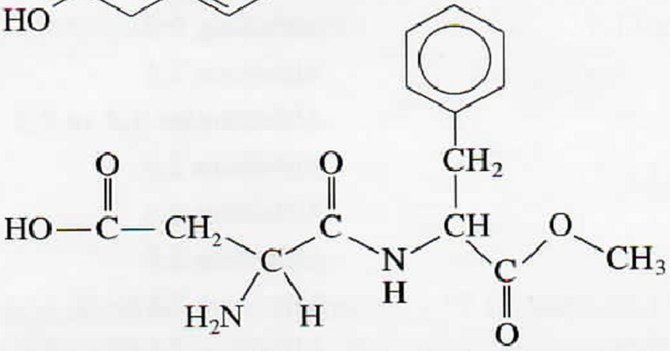
2.20 Aşağıdaki bileşiklerin her birindeki fonksiyonel grupların hepsini belirleyiniz

(a)



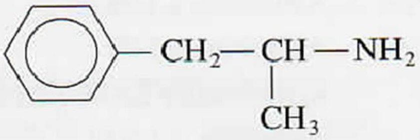
Vitamin D$_3$

(b)



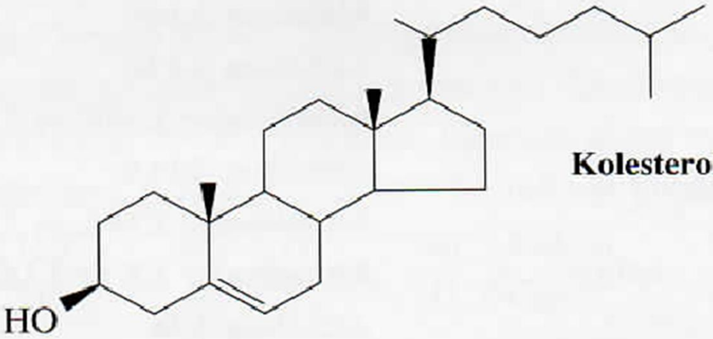
Aspartam

(c)



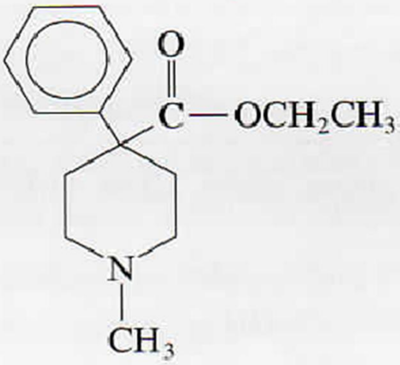
Amfetamin

(d)



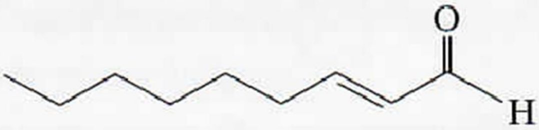
Kolesterol

(e)



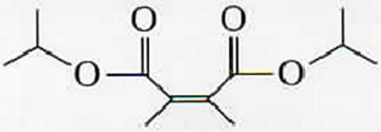
Demerol

(f)



Hıyarlarda bulunan bir hamamböceği kovucusu

(g)



Sentetik bir hamamböceği kovucusu

2.20 (a) Three carbon-carbon double bonds (alkene) and a 2° alcohol

(b) Phenyl, carboxylic acid, amide, ester, and a 1° amine

(c) Phenyl and a 1° amine

(d) Carbon-carbon double bond and a 2° alcohol

(e) Phenyl, ester, and a 3° amine

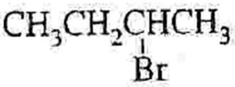
(f) Carbon-carbon double bond and an aldehyde

(g) Carbon-carbon double bond and 2 ester groups

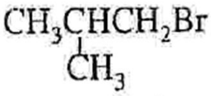
2.21 C_4H_9Br formülüne sahip dört alkil bromür vardır. Bunların yapı formüllerini yazınız ve her birini birincil, ikincil ya da üçüncül alkil bromür olarak sınıflandırınız.

2.21 $CH_3CH_2CH_2CH_2Br$

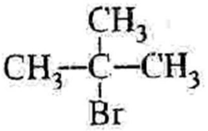
1° Alkyl halide


$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

2° Alkyl halide


$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Br$

1° Alkyl halide

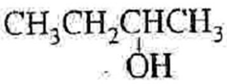

$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}-CH_3$

3° Alkyl halide

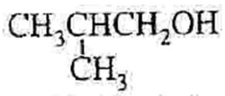
2.22 $C_4H_{10}O$ formülünde yedi izomerik bileşik vardır. Bunların yapılarını yazınız ve her bir bileşiği fonksiyonel grubuna göre sınıflandırınız.

2.22 $CH_3CH_2CH_2CH_2OH$

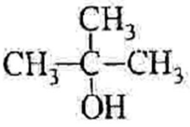
1° Alcohol


$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

2° Alcohol


$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$

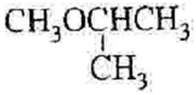
1° Alcohol


$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CH_3$

3° Alcohol

$CH_3OCH_2CH_2CH_3$

Ether


$CH_3O\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$

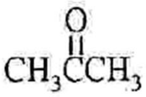
Ether

$CH_3CH_2OCH_2CH_3$

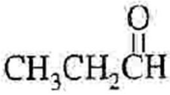
Ether

2.23 C_3H_6O formülündeki dört bileşiğin yapı formüllerini yazınız ve her birini fonksiyonel grubuna göre sınıflandırınız.

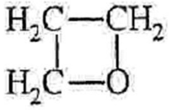
2.23 Any four of the following:


$CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_3$

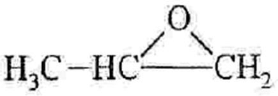
Ketone


$CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}H$

Aldehyde



Ether



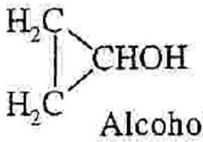
Ether

$CH_2{=}CHCH_2OH$

Alkene, alcohol

$CH_2{=}CH{-}O{-}CH_3$

Alkene, ether



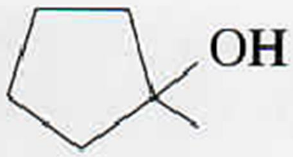
Alcohol

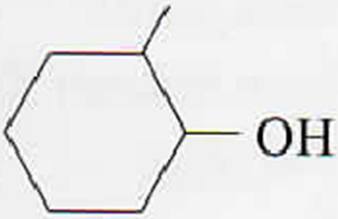
2.24 Aşağıdaki alkolleri birincil, ikincil ya da üçüncül olarak sınıflandırınız:

(a) $(CH_3)_3CCH_2OH$

(b) $CH_3CH(OH)CH(CH_3)_2$

(c) $(CH_3)_2C(OH)CH_2CH_3$

(d) 

(e) 

2.24 (a) 1° (b) 2° (c) 3° (d) 3° (e) 2°

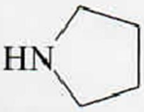
2.25 Aşağıdaki aminleri birincil, ikincil ya da üçüncül olarak sınıflandırınız:

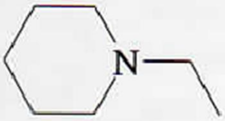
(a) $CH_3NHCH(CH_3)_2$

(b) $CH_3CH_2CH(CH_3)CH_2NH_2$

(c) $(CH_3CH_2)_3N$

(d) $(C_6H_5)_2CHCH_2NHCH_3$

(e) 

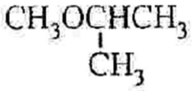
(f) 

2.25 (a) 2° (b) 1° (c) 3° (d) 2° (e) 2° (f) 3°

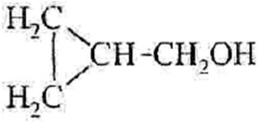
2.26 Aşağıdakilerden her birinin yapısal formülünü yazınız:

(a) $C_4H_{10}O$ formülüne sahip üç eter
(b) C_4H_8O formülüne sahip üç birincil alkol
(c) C_3H_6O formülüne sahip bir ikincil alkol
(d) C_4H_8O formülüne sahip bir üçüncül alkol
(e) $C_3H_6O_2$ formülüne sahip iki ester
(f) $C_5H_{11}Br$ formülüne sahip dört birincil alkil halojenür
(g) $C_5H_{11}Br$ formülüne sahip üç ikincil alkil halojenür
(h) $C_5H_{11}Br$ formülüne sahip bir üçüncül alkil halojenür
(i) $C_5H_{10}O$ formülüne sahip üç aldehit
(j) $C_5H_{10}O$ formülüne sahip üç keton
(k) C_3H_9N formülüne sahip iki birincil amin
(l) C_3H_9N formülüne sahip bir ikincil amin
(m) C_3H_9N formülüne sahip bir üçüncül amin
(n) C_2H_9NO formülüne sahip iki amit

2.26 (a) $CH_3OCH_2CH_2CH_3$

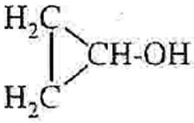

$CH_3OCH(CH_3)CH_3$

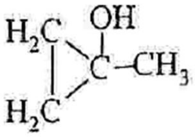
$CH_3CH_2OCH_2CH_3$

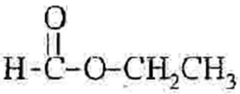
(b)


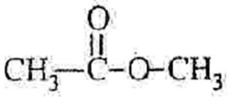
$CH_2{=}CHCH_2CH_2OH$

$CH_3CH{=}CHCH_2OH$

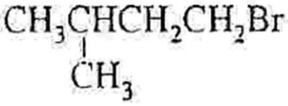
(c)


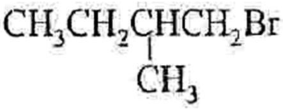
(d)


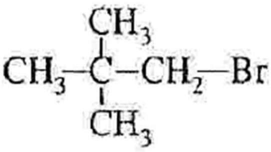
(e)

$H{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2CH_3$

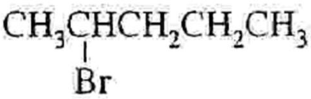

$CH_3{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_3$

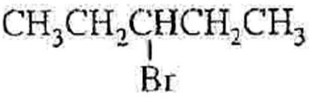
(f) $CH_3CH_2CH_2CH_2CH_2Br$

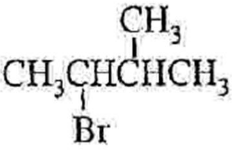

$CH_3CH(CH_3)CH_2CH_2Br$

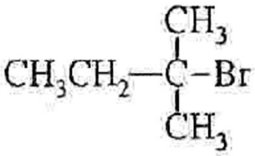

$CH_3CH_2CH(CH_3)CH_2Br$

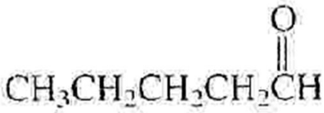

$CH_3{-}C(CH_3)_2{-}CH_2{-}Br$

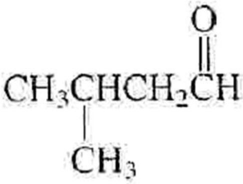
(g)

$CH_3CH(Br)CH_2CH_2CH_3$

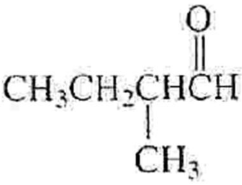

$CH_3CH_2CH(Br)CH_2CH_3$

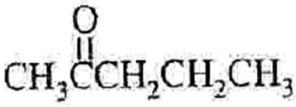

$CH_3CH(Br)CH(CH_3)CH_3$

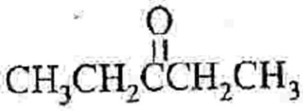
(h)

$CH_3CH_2{-}C(CH_3)_2{-}Br$

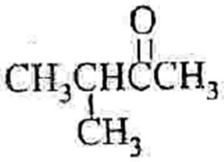
(i)

$CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}H$


$CH_3CH(CH_3)CH_2\overset{O}{\overset{\|}{C}}H$

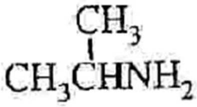

$CH_3CH_2CH(CH_3)\overset{O}{\overset{\|}{C}}H$

(j) 
$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$


$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$

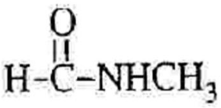

$CH_3\underset{CH_3}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}CH_3$

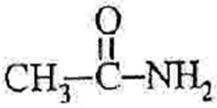
(k) $CH_3CH_2CH_2NH_2$


$CH_3\overset{CH_3}{\overset{|}{C}}HNH_2$

(l) $CH_3CH_2NHCH_3$

(m) $(CH_3)_3N$

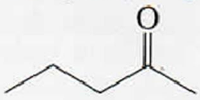
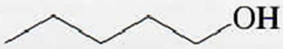
(n) 
$H-\overset{O}{\overset{\|}{C}}-NHCH_3$

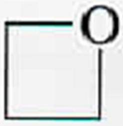
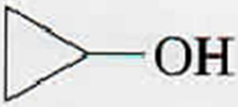

$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$

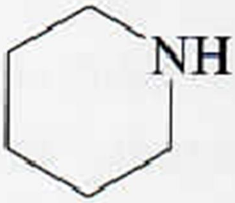
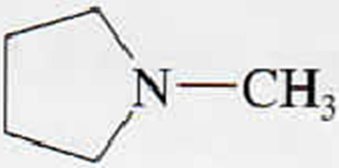
2.27 Aşağıdaki çiftlerdeki hangi bileşiğin kaynama noktası daha yüksektir? Cevabınızı açıklayınız.

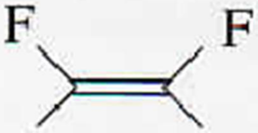
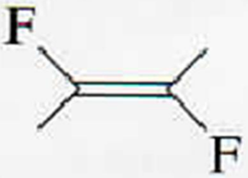
(a) $CH_3CH_2CH_2OH$ ya da $CH_3CH_2OCH_3$

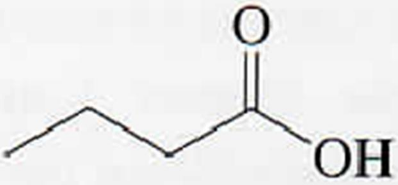
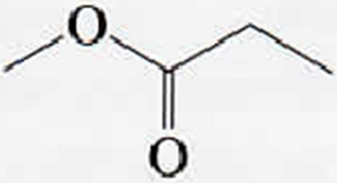
(b) $CH_3CH_2CH_2OH$ ya da $HOCH_2CH_2OH$

(c)  ya da 

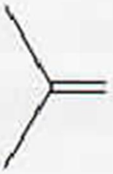
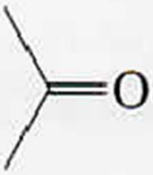
(d)  ya da 

(e)  ya da 

(f)  ya da 

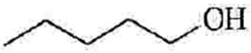
(g)  ya da 

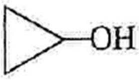
(h) Heksan, $CH_3(CH_2)_4CH_3$ veya nonan, $CH_3(CH_2)_7CH_3$

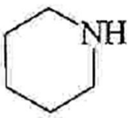
(i)  ya da 

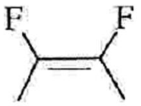
2.27 (a) $CH_3CH_2CH_2OH$ because its molecules can form hydrogen bonds to each other through its $-\ddot{\underset{..}{O}}-H$ group.

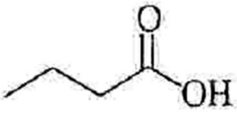
(b) $HOCH_2CH_2OH$ because with two $-\ddot{\underset{..}{O}}-H$ groups, its molecules can form more hydrogen bonds with each other.

(c)  because its molecules can form hydrogen bonds to each other.

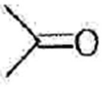
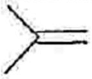
(d)  [Same reason as (c)].

(e)  because its molecules can form hydrogen bonds to each other through its $-\ddot{\underset{|}{N}}-H$ group.

(f)  because its molecules will have a larger dipole moment. (The trans compound will have $\mu = 0$.)

(g)  [Same reason as (c)].

(h) Nonane, because of its larger molecular weight and larger size, will have larger van der Waals attractions.

(i)  because its carbonyl group is far more polar than the double bond of .

2.28 Problem 2.27 deki a,c,d,e,g ve i çiftlerindeki her bir bileşiğin diğerinden farklılığını belirleyecek başlıca İR soğurma bandlarını öngörünüz.

2.28 (a) The alcohol would have a broad absorption from the O—H group in the 3200 to 3500 cm^{-1} region of its IR spectrum. The ether would have no such absorption.

(c) The ketone would have a strong absorption from its carbonyl group near 1700 cm^{-1} in its IR spectrum. The alcohol would have a broad absorption due to its hydroxyl group in the 3200 to 3500 cm^{-1} region of its IR spectrum.

(d) Same rationale as for (a)

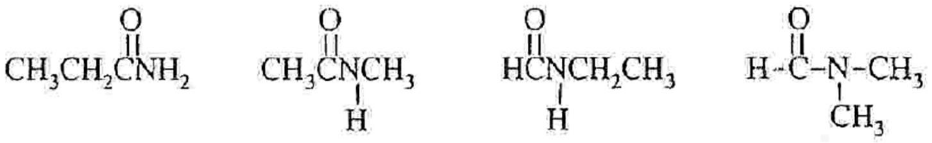
(e) The secondary amine would have an absorption near 3300 to 3500 cm^{-1} arising from N—H stretching. The tertiary amine would have no such absorption in this region since there is no N—H group present.

(g) Both compounds would exhibit absorptions near 1710 to 1780 cm^{-1} due to carbonyl stretching vibrations. The carboxylic acid would also have a broad absorption somewhere between 2500 and 3500 cm^{-1} due to its hydroxyl group. The ester would not have a hydroxyl absorption.

(i) The ketone would have a strong absorption from its carbonyl group near 1700 cm^{-1} in its IR spectrum. The alkene would have no such absorption but would have an absorption between 1620 and 1680 cm^{-1} due to C=C stretching.

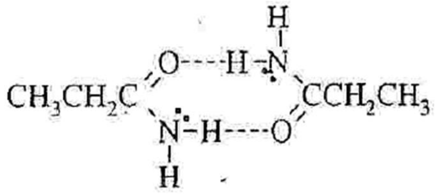
2.29 C_3H_7NO formülünde dört amit vardır. **(a)** Yapılarını yazınız. **(b)** Bu amitlerden birinin erime ve kaynama noktası diğer üçünden oldukça düşüktür. Bu amit hangisidir? Cevabınızı açıklayınız.

2.29 (a)

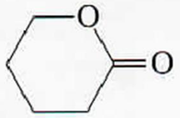


$CH_3CH_2\overset{O}{\overset{\|}{C}}NH_2$ $\quad CH_3\overset{O}{\overset{\|}{C}}\underset{\underset{H}{|}}{N}CH_3$ $\quad H\overset{O}{\overset{\|}{C}}\underset{\underset{H}{|}}{N}CH_2CH_3$ $\quad H-\overset{O}{\overset{\|}{C}}-\underset{\underset{CH_3}{|}}{N}-CH_3$

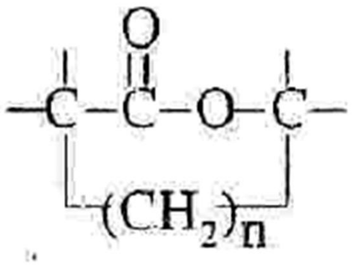
(b) The last one given above [i.e., $H\overset{O}{\overset{\|}{C}}N(CH_3)_3$] because it does not have a hydrogen that is covalently bonded to nitrogen and, therefore, its molecules cannot form hydrogen bonds to each other. The other molecules all have a hydrogen covalently bonded to nitrogen and, therefore, hydrogen-bond formation is possible. With the first molecule, for example, hydrogen bonds could form in the following way:



2.30 Aşağıda gösterilen genel yapıdaki halkalı bileşiklere laktonlar denir. Laktonda hangi fonksiyonel grup vardır.



2.30 An ester group,



$-\overset{|}{C}-\overset{O}{\overset{\|}{C}}-O-\overset{|}{C}-$ $\quad (CH_2)_n$

2.31 Hidrojen florürün dipol momenti 1,82 D; kaynama noktası 19,34 °C dur. Etil florürün (CH_3CH_2F) tamamen aynı dipol momenti ve daha büyük molekül kütlesi olmasına karşın kaynama noktası –37,7 °C dur Açıklayınız.

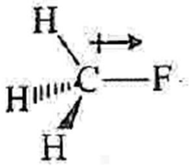
2.31 The attractive forces between hydrogen fluoride molecules are the very strong dipole–dipole attractions that we call *hydrogen bonds*. (The partial positive charge of a hydrogen fluoride molecule is relatively exposed because it resides on the hydrogen nucleus. By contrast, the positive charge of an ethyl fluoride molecule is buried in the ethyl group and is shielded by the surrounding electrons. Thus the positive end of one hydrogen fluoride molecule can approach the negative end of another hydrogen fluoride molecule much more closely, with the result that the attractive force between them is much stronger.)

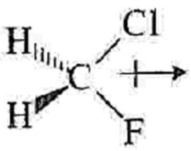
2.32 **Aşağıdaki çözücülerden hangisi iyonik bileşikleri çözebilir?**
(a) sıvı SO_2 **(b)** sıvı NH_3 **(c)** benzen **(d)** CCl_4

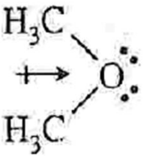
2.32 (a) and (b) are polar and hence are able to dissolve ionic compounds. (c) and (d) are nonpolar and will not dissolve ionic compounds.

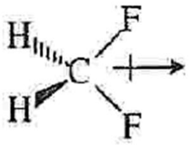
2.33 Kama – kesikli kama – çizgi gösterimini kullanarak aşağıdaki moleküllerden her birinin üç boyutlu formülünü yazınız. Eğer molekülün net dipol momenti varsa yönünü okla, +→, belirtiniz. Eğer net dipol momenti yoksa bunu da belirtiniz. (Bu tür basit problemlerde C—H bağının küçük polarlığını ihmal edebilirsiniz)

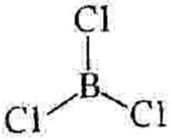
(a) CH_3F **(c)** CHF_3 **(e)** CH_2FCl **(g)** BeF_2 **(ı)** CH_3OH
(b) CH_2F_2 **(d)** CF_4 **(f)** BCl_3 **(h)** CH_3OCH_3 **(i)** CH_2O

2.33 (a)


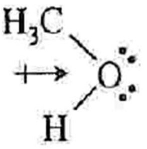
(e)


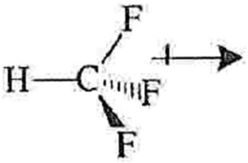
(h)


(b)


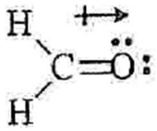
(f)


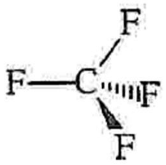
No dipole moment

(i)


(c)


(g) F—Be—F No dipole moment

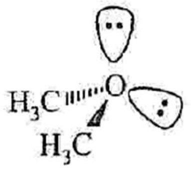
(j)


(d)


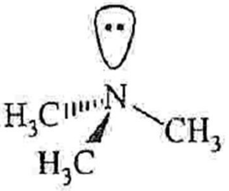
No dipole moment

2.34 Aşağıdaki molekülleri gözden geçiriniz: **(a)** dimetil eter, $(CH_3)_2O$, **(b)** trimetilamin, $(CH_3)_3N$, **(c)** trimetilbor, $(CH_3)_3B$ ve **(d)** dimetilberilyum $(CH_3)_2Be$. Her bir molekülün merkez atomunun (O, N, B ya da Be) melezleşme halini belirtiniz, merkez atomundaki bağ açılarının ne kadar olacağını söyleyiniz ve molekülün dipol momenti olup olmayacağını açıklayınız.

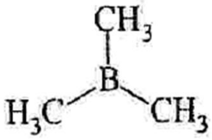
2.34 (a) Dimethyl ether: There are four electron pairs around the central oxygen: two bonding pairs and two nonbonding pairs. We would expect *sp*^{3} hybridization of the oxygen with a bond angle of approximately 109.5° between the methyl groups.



(b) Trimethylamine: There are four electron pairs around the central nitrogen: three bonding pairs and one nonbonding pair. We would expect *sp*^{3} hybridization of the nitrogen with a bond angle of approximately 109.5° between the methyl groups.



(c) Trimethylboron: There are only three bonding electron pairs around the central boron. We would expect *sp*^{2} hybridization of the boron with a bond angle of 120° between the methyl groups.



(d) Dimethylberyllium: There are only two bonding electron pairs around the central beryllium atom. We would expect *sp* hybridization of the beryllium atom with a bond angle of 180° between the methyl groups.

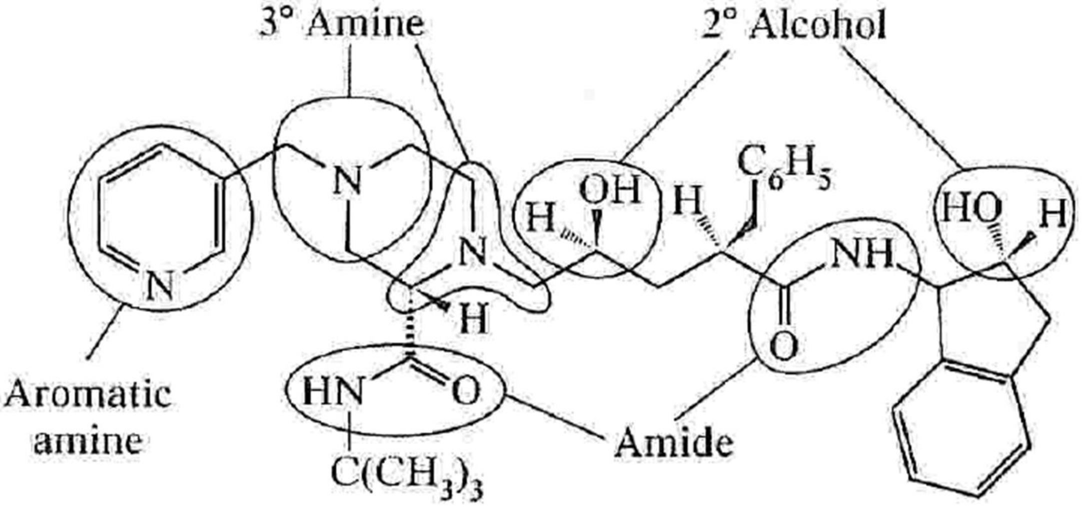
$H_3C{-}Be{-}CH_3$

2.35 **Bu açıklamayı irdeleyiniz: polar bir molekül için polar bağların bulunması gereklidir, ancak bu gereksinim yeterli değildir.**

2.35 Without one (or more) polar bonds, a molecule cannot possess a dipole moment and, therefore, it cannot be polar. If the bonds are directed so that the bond moments cancel, however, the molecule will not be polar even though it has polar bonds.

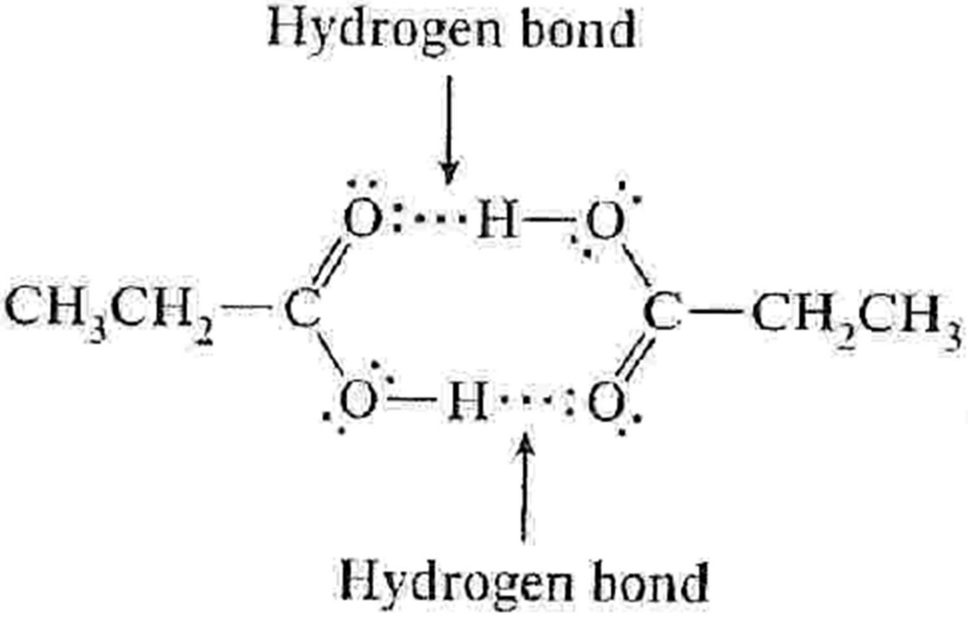
2.36 **Crixivanın bütün fonksiyonel gruplarını belirtiniz. (Crixivanın yapısı bu bölümün başında gösterilmiştir).**

2.36 Crixivan has the following functional groups:



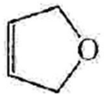
2.37 Propanoik asitin İR spektrumu (Şekil 2.16) karboksilik asit fonksiyonel grubunun hidrojen bağlı O — H gerilme soğurmasını göstermektedir. İki propanoik asit molekülünün hidrojen bağıyla nasıl dimerleştiğini gösteren yapıları yazınız.

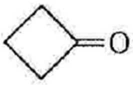
2.37

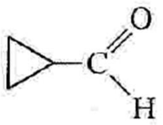


* **2.38** C_4H_6O molekül formülündeki iki izomerin yapıları simetriktir. CCl_4 (polar olmadığı için kullanılmıştır) içerisinde seyreltik çözeltide her iki izomerin infrared spektrumlarında 3600 cm^{-1} bölgesinde soğurma yoktur. İzomer A'nın yaklaşık 3080, 1620 ve 700 cm^{-1} de soğurma bandları vardır. İzomer B'nin ise 2900 cm^{-1} bölgesinde ve 1780 cm^{-1}'de bandları vardır. A için bir ve B için iki olası yapı öneriniz.

*2.38


A

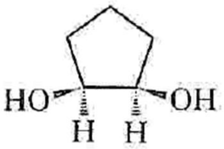

B

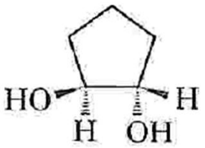

B′

The 1780-cm^{-1} band is in the general range for C=O stretching so structure B′ is considered one of the possible answers, but only B would have its C=O stretch at this high frequency (B′ would be at about 1730 cm^{-1}).

*** 2.39** Eğer iki sübstitüent halka iskeletinin aynı tarafındaysa *cis*, zıt tarafındaysa *trans* (bu terimler 1,2-disübstitüe alken izomerlerinde kullanılan terimlerle aynıdır) olarak adlandırılır. 1,2-Siklopentandiolün (5 atomlu halkası ve iki komşu karbonda biri cis diğeri trans olan iki izomer bileşik) steroizomerlerini göz önüne alınız. CCl_4 içinde oldukça seyreltik çözeltide her iki izomerin yaklaşık 3626 cm^{-1} de infrared soğurma bandı olmasına karşın 3572 cm^{-1} de sadece bir izomerin bandı vardır. **(a)** Siklopentan halkasının düzlemsel olduğunu (bu konunun ayrıntısı ileride incelenecektir) düşününüz ve kama–kesikli kama yöntemini kullanarak OH gruplarını gösteren iki izomerik yapıyı çiziniz. **(b)** Hangi izomerin 3572 cm^{-1} bandı olduğunu belirleyiniz ve nedenini açıklayınız.

*2.39 (a)

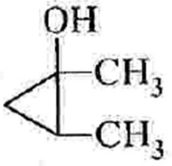

cis


trans

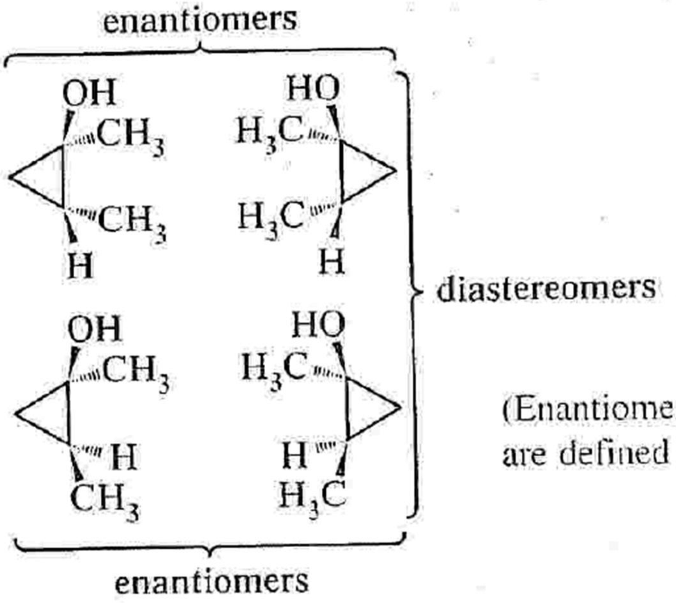
(b) The *cis* isomer will have the 3572-cm^{-1} band because only in it are the two hydroxyl groups close enough to permit intramolecular hydrogen-bonding. (Intermolecular hydrogen-bonding is not possible at high dilution in a non-polar solvent like CCl_4.)

***2.40** C bileşiği asimetriktir, molekül formülü $C_5H_{10}O$'dur, iki metil grubu ve bir 3° fonksiyonel grup içermektedir. 3200–3550-cm^{-1} bölgesinde geniş bir infrared soğurma bandı vardır ve 1620–1680-cm^{-1} bölgesinde soğurma bandı yoktur. **(a)** C için bir yapı öneriniz **(b)** Önerdiğiniz yapının steroizomerleri olabilir mi? Olabilirse kama–kesikli kama yöntemini kullanarak steroizomerlerin yapısını çiziniz.

***2.40** (a)



(b)



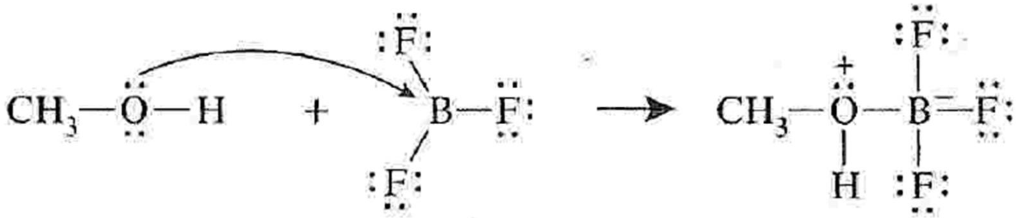
(Enantiomers and diastereomers are defined in Chapter 5.)

Organik Tepkimelere Giriş: Asitler ve Bazlar

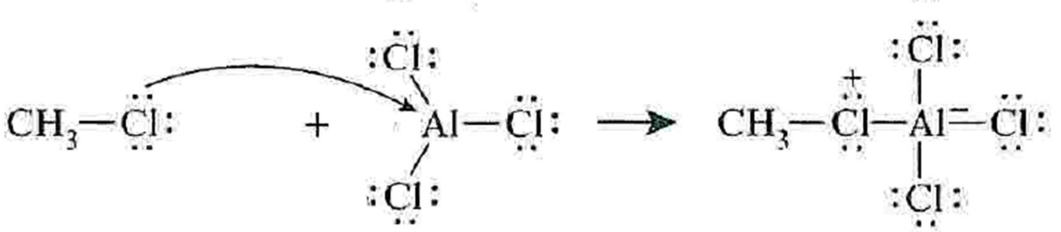
Problem 3.1

(a) Metil alkolün BF_3 ile
(b) Metil klorürün $AlCl_3$ ile
(c) Dimetil eterin BF_3 ile
meydana gelen Lewis asit–baz tepkimelerine ait eşitliklerini yazınız.

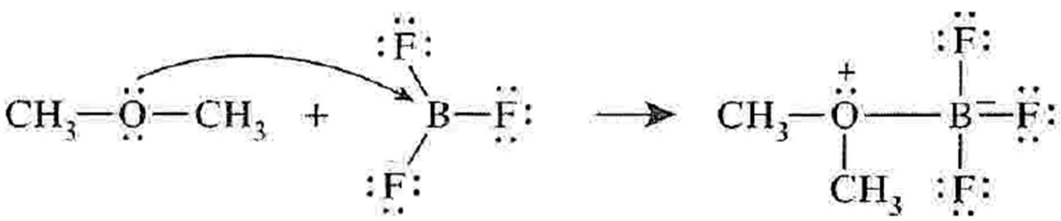
3.1 (a)



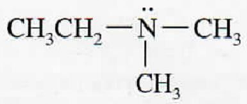
(b)

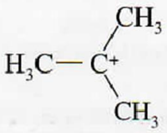


(c)



Aşağıdakilerden hangileri potansiyel Lewis asidi, hangileri potansiyel Lewis bazıdır? **Problem 3.2**

(a) 
$CH_3CH_2-\ddot{N}(CH_3)-CH_3$

(b) 
$H_3C-C^+(CH_3)_2$

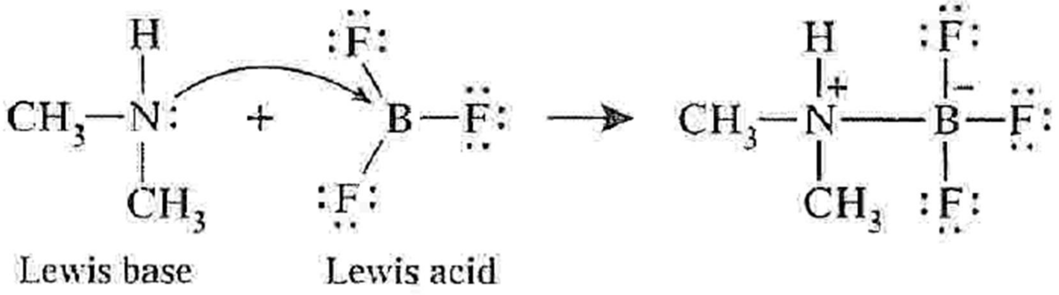
(c) $(C_6H_5)_3P$: (d) $:\ddot{Br}:^-$ (e) $(CN_3)_3B$ (f) $H:^-$

3.2 (a) Lewis base (b) Lewis acid

(c) Lewis base (d) Lewis base

(e) Lewis acid (f) Lewis base

Problem 3.3 Dimetilamin ve bor triflorür arasında olabilecek tepkimeyi yazmak için eğri ok gösterimini kullanınız. Lewis asit ve Lewis bazını belirtiniz. Uygun formal yükleri belirleyiniz.

3.3 

Formik asit (HCO_2H) için $K_a = 1{,}76 \times 10^{-4}$'tür. (a) Formik asitin 0,1*M* sulu çözeltisindeki hidronyum ve format iyonlarının (HCO_2^-) molar derişimi nedir? (b) Formik asitin yüzde kaçı iyonlaşmıştır? **Problem 3.4**

3.4 (a) $$K_a = \frac{[H_3O^+][HCO_2^-]}{[HCO_2H]} = 1.77 \times 10^{-4}$$

Let $x = [H_3O^+] = [HCO_2^-]$ at equilibrium
then, $0.1 - x = [HCO_2H]$ at equilibrium
but, since the K_a is very small, x will be very small and $0.1 - x \cong 0.1$
Therefore,

$$\begin{aligned} \frac{(x)(x)}{0.1} &= 1.77 \times 10^{-4} \\ x^2 &= 1.77 \times 10^{-5} \\ x &= 0.0042 = [H_3O^+] = [HCO_2^-] \end{aligned}$$

(b) $$\% \text{ Ionized} = \frac{[H_3O^+]}{0.1} \times 100 \quad \text{or} \quad \frac{[HCO_2^-]}{0.1} \times 100$$

$$= \frac{.0042}{0.1} \times 100 = 4.2\%$$

Problem 3.5 ➤ (a) Bir asidin (HA) K_a'sı 10^{-7}'dir. Bu asidin pK_a'sı nedir? (b) Bir başka asidin (HB) K_a'sı 5'tir; pK_a'sı nedir? (c) Hangisi daha kuvvetli asittir?

3.5 (a) $pK_a = -\log 10^{-7} = -(-7) = 7$

(b) $pK_a = -\log 5.0 = -0.699$

(c) Since the acid with a $K_a = 5$ has a larger K_a, it is the stronger acid.

Problem 3.6 ➤ Hidronyum iyonunun (H_3O^+) pK_a'sının Çizelge 3.1'de verildiği gibi –1,74 olduğunu hesaplamaları göstererek kanıtlayınız.

3.6 When H_3O^+ acts as an acid in aqueous solution, the equation is

$$H_3O^+ + H_2O \leftrightarrows H_2O + H_3O^+$$

and K_a is

$$K_a = \frac{[H_2O][H_3O^+]}{[H_3O^+]} = [H_2O]$$

The molar concentration of H_2O in pure H_2O, that is, $[H_2O] = 55.5$; therefore, $K_a = 55.5$

The pK_a is

$$pK_a = -\log 55.5 = -1.74$$

Problem 3.7 ➤ Anilinyum iyonunun ($C_6H_5NH_3^+$) pK_a'sı 4,6'dır. Buna göre anilinin metilaminden daha kuvvetli baz olup olmadığına karar veriniz.

3.7 The pK_a of the methylaminium ion is equal to 10.6 (Section 3.5C). Since the pK_a of the anilinium ion is equal to 4.6, the anilinium ion is a stronger acid than the methylaminium ion, and aniline ($C_6H_5NH_2$) is a weaker base than methylamine (CH_3NH_2).

Problem 3.8 ➤ Aşağıdaki tepkimelerin her biri için entropi değişimin, $\Delta S°$, pozitif mi, negatif mi veya yaklaşık sıfır mı olacağını umarsınız? (Tepkimelerin gaz fazında meydana geldiklerini kabul ediniz.)
(a) $A + B \longrightarrow C$ **(b)** $A + B \longrightarrow C + D$ **(c)** $A \longrightarrow B + C$

3.8 (a) Negative. Because the atoms are constrained to one molecule in the product, they have to become more ordered.

(b) Approximately zero.

(c) Positive. Because the atoms are in two separate product molecules, they become more disordered.

Problem 3.9 ➤ (a) $K_{denge} = 1$ bir olan tepkime için $\Delta G°$ değeri nedir? (b) $K_{denge} = 10$ olduğunda? (Denge sabitini on misli arttırmak için gerekli olan $\Delta G°$ değişimi, hatırlamak için uygun bir ifadedir.) (c) Bu tepkime için entropi değişiminin ihmal edilebilir (veya sıfır) olduğunu kabul ederek denge sabitinin on misli arttırılması için gerekli $\Delta H°$ değişimi nedir?

3.9 (a) If $K_{eq} = 1$

then,

$$\log K_{eq} = 0 = \frac{-\Delta G°}{2.303RT}$$

$$\Delta G° = 0$$

(b) If $K_{eq} = 10$

then,

$$\log K_{eq} = 1 = \frac{-\Delta G°}{2.303RT}$$

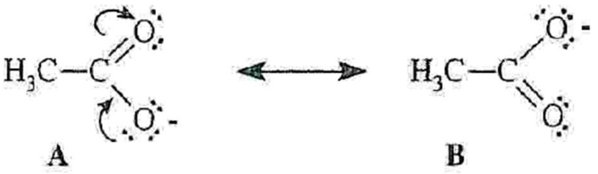
$$\Delta G° = -(2.303)(0.008314\ \text{kJ mol}^{-1}\ \text{K}^{-1})(298\ \text{K}) = -5.71\ \text{kJ mol}^{-1}$$

(c) $\Delta G° = \Delta H° - T\Delta S°$

$$\Delta G° = \Delta H° = -5.71\ \text{kJ mol}^{-1} \text{ if } \Delta S° = 0$$

Rezonans teorisi, bir karboksilik asidin asitliğinin en iyi açıklamasını sağlayabilir veya sağlayamaz, ancak, iki ilgili gerçeğe uygun bir açıklama getirir: Asetat iyonundaki karbon–oksijen bağ uzunlukları aynıdır ve asetat iyonunun oksijenleri eşit negatif yüklere sahiptir. Bu gerçekleri rezonansla açıklayınız. ◄ **Problem 3.10**

3.10 Structures **A** and **B** make equal contributions to the overall hybrid. This means that the carbon-oxygen bonds should be the same length and that the oxygens should bear equal positive charges.



Problem 3.11 ➤ Aşağıda verilenlerden hangisinin daha kuvvetli asit olmasını beklersiniz? Her bir durumda gerekçenizi açıklayınız.

(a) CH_2ClCO_2H veya $CHCl_2CO_2H$

(b) CCl_3CO_2H veya $CHCl_2CO_2H$

(c) CH_2FCO_2H veya CH_2BrCO_2H

(d) CH_2FCO_2H veya $CH_2FCH_2CO_2H$

3.11 (a) $CHCl_2CO_2H$ would be the stronger acid because the electron-withdrawing inductive effect of *two chlorine atoms* would make its hydroxyl proton more positive. The electron-withdrawing effect of the two chlorine atoms would also stabilize the dichloroacetate ion more effectively by dispersing its negative charge more extensively.

(b) CCl_3CO_2H would be the stronger acid for reasons similar to those given in (a), except here there are three versus two electron-withdrawing chlorine atoms involved.

(c) CH_2FCO_2H would be the stronger acid because the electron-withdrawing effect of a fluorine atom is greater than that of a bromine atom (fluorine is more electronegative).

(d) CH_2FCO_2H is the stronger acid because the fluorine atom is nearer the carboxyl group and is, therefore, better able to exert its electron-withdrawing inductive effect. (*Remember:* Inductive effects weaken steadily as the distance between the substituent and the group increases.)

Problem 3.12

Oksijen, azot veya bir çoklu bağ içeren herhangi bir organik bileşiğin derişik sülfürik asitte çözüneceği genel bir kuraldır. Bu kuralın dayanağını açıklayınız.

3.12 All compounds containing oxygen and most compounds containing nitrogen will have an unshared electron pair on their oxygen or nitrogen atom. These compounds can, therefore, act as bases and accept a proton from concentrated sulfuric acid. When they accept a proton, these compounds become either oxonium ions or ammonium ions, and having become ionic, they are soluble in the polar medium of sulfuric acid. The only nitrogen compounds that do not have an electron pair on their nitrogen atom are quaternary ammonium compounds, and these, already being ionic, also dissolve in the polar medium of concentrated sulfuric acid.

Problem 3.13

Aşağıdaki bileşiklerin veya çözeltilerin her biri karıştırıldığında meydana gelebilecek asit–baz tepkimelerinin eşitliklerini yazınız. Uygun pK_a değerlerini kullanarak (Çizelge 3.1) her bir durumda daha kuvvetli asit ve daha kuvvetli baz ile daha zayıf asit ve daha zayıf bazı belirtiniz. (Eğer bir asit–baz tepkimesi meydana gelemeyecekse bunu belirtmelisiniz.)

(a) CH_3OH'ye NaH eklendiğinde

(b) CH_3CH_2OH'ye $NaNH_2$ eklendiğinde

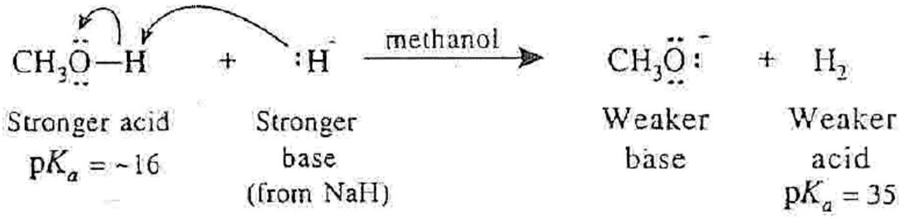
(c) Heksan içerisindeki etillityum çözeltisine NH_3 gazı eklendiğinde

(d) Sıvı amonyak içerisindeki sodyum amit çözeltisine NH_4Cl eklendiğinde

(e) H_2O'ya $(CH_3)_3CONa$ eklendiğinde

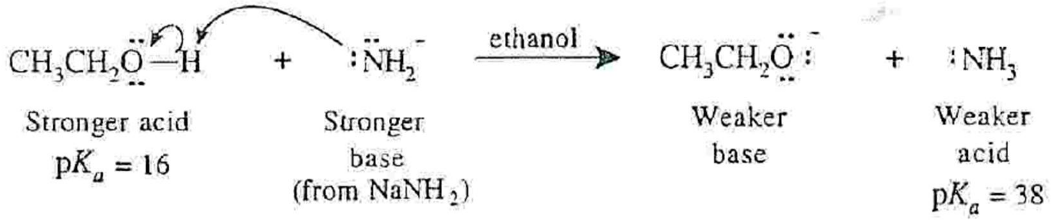
(f) $(CH_3)_3COH$'ye NaOH eklendiğinde

3.13 (a)



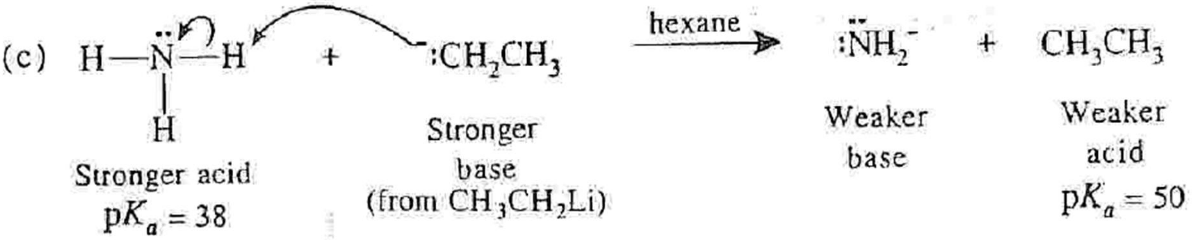
$$CH_3\ddot{O}-H + :H^- \xrightarrow{\text{methanol}} CH_3\ddot{O}:^- + H_2$$

(b)



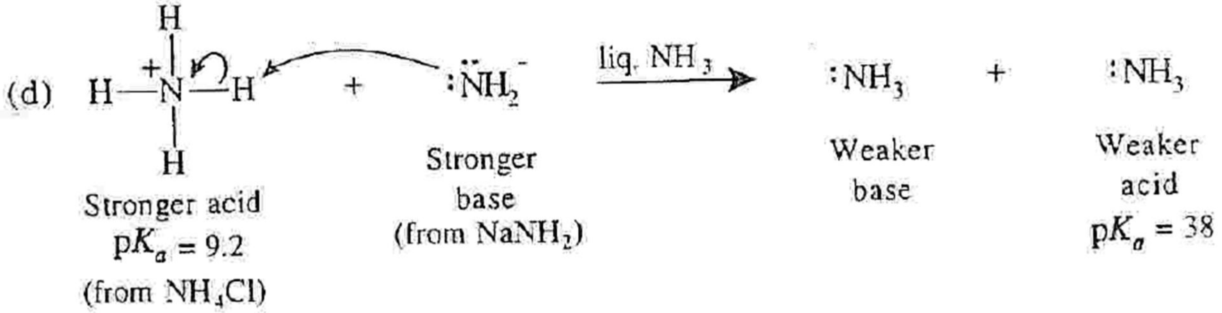
$$CH_3CH_2\ddot{O}-H + :\ddot{N}H_2^- \xrightarrow{\text{ethanol}} CH_3CH_2\ddot{O}:^- + :NH_3$$

(c)



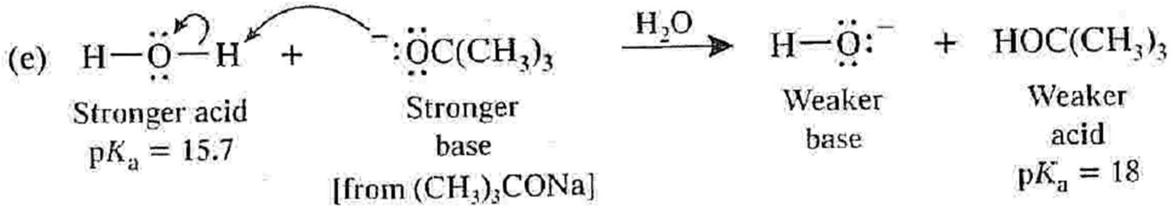
$$H_2N{-}H + {:}CH_2CH_3 \xrightarrow{\text{hexane}} {:}NH_2^- + CH_3CH_3$$

(d)



$$H_3\overset{+}{N}{-}H + {:}NH_2^- \xrightarrow{\text{liq. } NH_3} {:}NH_3 + {:}NH_3$$

(e)



$$H{-}O{-}H + {^-}{:}OC(CH_3)_3 \xrightarrow{H_2O} H{-}O{:}^- + HOC(CH_3)_3$$

(f) No appreciable acid-base reaction would occur because NaOH is not a strong enough base to remove a proton from $(CH_3)_3COH$.

Problem 1.1 ➤ Aşağıdaki asit-baz tepkimelerini tamamlayınız.

(a) $CH_3C{\equiv}CH + NaH \xrightarrow{\text{heksan}}$

(b) (a)' da elde edilen çözelti $+ D_2O \longrightarrow$

(c) $CH_3CH_2Li + D_2O \xrightarrow{\text{heksan}}$

(d) $CH_3CH_2OH + NaH \xrightarrow{\text{heksan}}$

(e) (d)' de elde edilen çözelti $+ T_2O \longrightarrow$

(f) $CH_3CH_2CH_2Li + D_2O \xrightarrow{\text{heksan}}$

3.14 (a) $HC{\equiv}CH + NaH \xrightarrow{\text{hexane}} HC{\equiv}CNa + H_2$

(b) $HC{\equiv}CNa + D_2O \xrightarrow{\text{hexane}} HC{\equiv}CD + NaOD$

(c) $CH_3CH_2Li + D_2O \xrightarrow{\text{hexane}} CH_3CH_2D + LiOD$

(d) $CH_3CH_2OH + NaH \xrightarrow{\text{hexane}} CH_3CH_2ONa + H_2$

(e) $CH_3CH_2ONa + T_2O \xrightarrow{\text{hexane}} CH_3CH_2OT + NaOT$

(f) $CH_3CH_2CH_2Li + D_2O \xrightarrow{\text{hexane}} CH_3CH_2CH_2D + LiOD$

3.15 Aşağıdaki asitlerin her birinin konjuge bazı nedir?

(a) NH_3
(b) H_2O
(c) H_2
(d) $HC{\equiv}CH$
(e) CH_3OH
(f) CH_3OH

3.15 (a) $:\ddot{N}H_2^-$ (the amide ion) (d) $H-C\equiv C:^-$ (the ethynide ion)

(b) $H-\ddot{\underset{\cdot\cdot}{O}}:^-$ (the hydroxide ion) (e) $CH_3\ddot{\underset{\cdot\cdot}{O}}:^-$ (the methoxide ion)

(c) $:H^-$ (the hydride ion) (f) H_2O (water)

3.16 Problem 3.15 de cevap olarak verdiğiniz bazları azalan bazikliklerine göre sıralayın.

3.16 $:\ddot{N}H_2^- > :H^- > H-C\equiv C:^- > CH_3\ddot{\underset{\cdot\cdot}{O}}:^- \approx H-\ddot{\underset{\cdot\cdot}{O}}:^- > H_2O$

3.17 Aşağıdaki bazların her birinin konjuge asidi nedir?

(a) HSO_4^- **(c)** CH_3NH_2 **(e)** $CH_3CH_2^-$

(b) H_2O **(d)** NH_2 **(f)** $CH_3CO_2^-$

3.17 (a) H_2SO_4 (d) NH_3

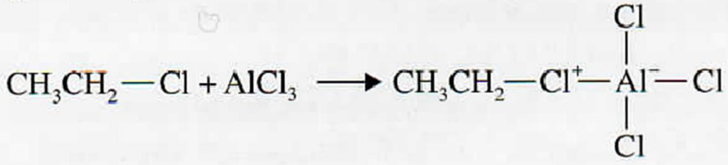
(b) H_3O^+ (e) CH_3CH_3

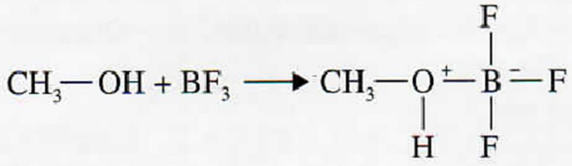
(c) $CH_3NH_3^+$ (f) CH_3CO_2H

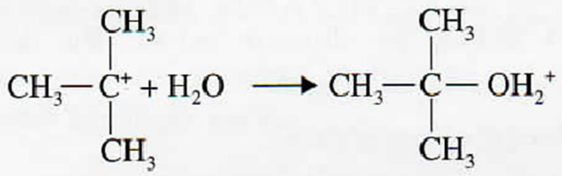
3.18 Problem 3.17'de cevap olarak verdiğiniz asitleri azalan asitliklerine göre sıralayınız.

3.18 $H_2SO_4 > H_3O^+ > CH_3CO_2H > CH_3NH_3^+ > NH_3 > CH_3CH_3$

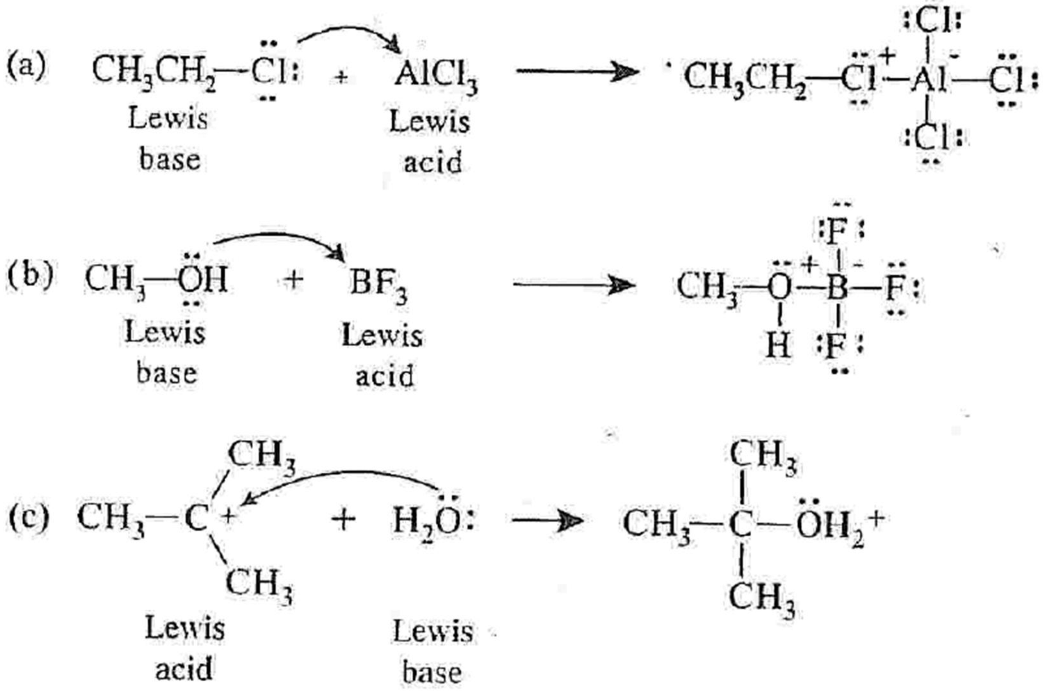
3.19 Aşağıdaki tepkimelerin her birinde Lewis asit ve Lewis bazını belirtiniz.

(a)

$CH_3CH_2-Cl + AlCl_3 \longrightarrow CH_3CH_2-Cl^{+}-\underset{Cl}{\overset{Cl}{Al^{-}}}-Cl$

(b)

$CH_3-OH + BF_3 \longrightarrow CH_3-\underset{H}{O^{+}}-\underset{F}{\overset{F}{B^{-}}}-F$

(c)

$CH_3-\underset{CH_3}{\overset{CH_3}{C^{+}}} + H_2O \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH_2^{+}$

3.19

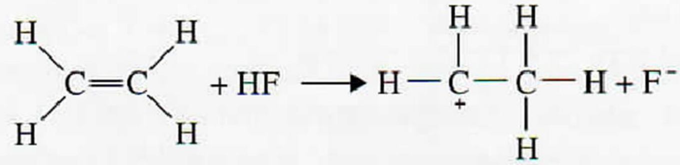


3.20 Aşağıdaki tepkimeleri eğri oklar ve bütün paylaşılmamış elektron çiftlerini de göstererek yeniden yazınız.

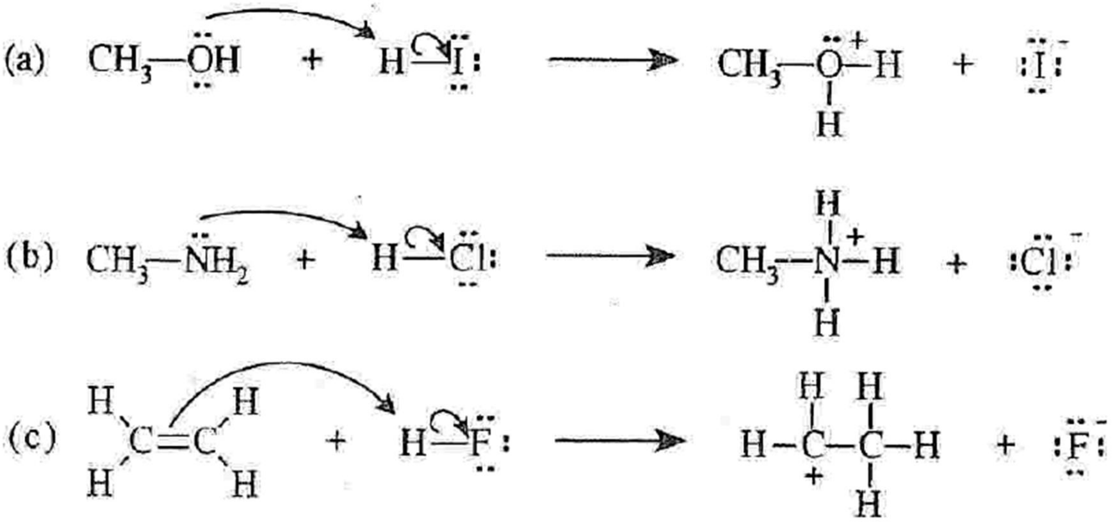
(a) $CH_3OH + HI \longrightarrow CH_3OH_2^+ + I^-$

(b) $CH_3NH_2 + HCl \longrightarrow CH_3NH_3^+ + Cl^-$

(c)



3.20

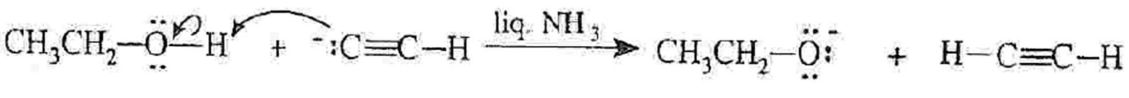


3.21 Metil alkol NaH ile etkileştirildiğinde ürün $CH_3O^-\ Na^+$ (ve H_2)'dir, $Na^+\ ^-CH_2OH$ (ve H_2) değildir. Bunun niçin böyle olduğunu açıklayınız.

3.21 Because the proton attached to the highly electronegative oxygen atom of CH_3OH is much more acidic than the protons attached to the much less electronegative carbon atom.

3.22 $HC\equiv C{:}^-Na^+$'nın sıvı amonyaktaki çözeltisine etil alkol eklenirse nasıl bir tepkime meydana gelecektir?

3.22



3.23 **(a)** Formik asitin (HCO_2H) K_a'sı $1{,}77 \times 10^{-9}$'dur, pK_a'sı nedir? **(b)** pK_a'sı 13 olan bir asidin K_a'sı nedir?

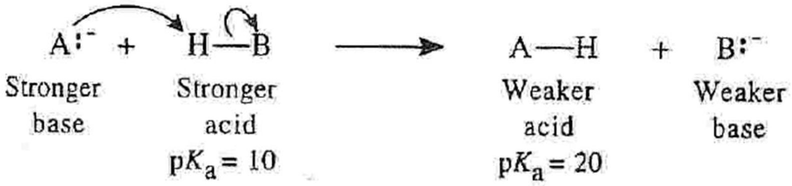
3.23 (a) $pK_a = -\log 1.77 \times 10^{-4} = 4 - 0.248 = 3.752$

(b) $K_a = 10^{-13}$

3.24 Ha asidinin pK_a'sı 20 ; HB asidinin pK_a'sı 10'dur. **(a)** Hangisi daha kuvvetli asittir? **(b)** HB'ye Na^+A^- eklenirse sağa doğru kayan bir asit–baz denge tepkimesi meydana gelecek midir? Cevabınızı açıklayınız.

3.24 (a) HB is the stronger acid because it has the smaller pK_a.

(b) Yes. Since A^- is the stronger base and HB is the stronger acid, the following acid-base reaction will take place.



3.25 Aşağıdakilerin her biri karıştırıldığında meydana gelecek olan asit–baz tepkimelerinin eşitliklerini eğri oklar kullanarak yazınız. Eğer denge tercih edilemediğinden belirgin bir asit baz tepkimesi meydana gelmezse bunu belirtmelisiniz.

(a) Sulu NaOH ve $CH_3CH_2CO_2H$

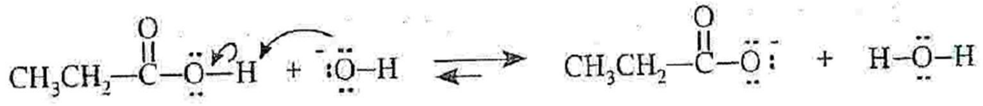
(b) Sulu NaOH ve $C_6H_5SO_3H$

(c) Etil alkol içinde CH_3CH_2ONa ve etin

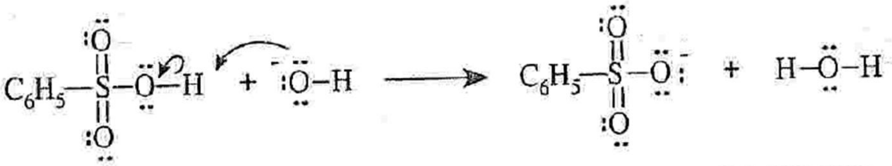
(d) Heksan içerisinde CH_3CH_2Li ve etin

(e) Heksan içerisinde CH_3CH_2Li ve etil alkol

3.25 (a)

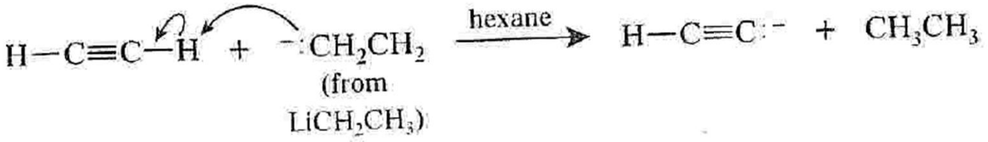


(b)

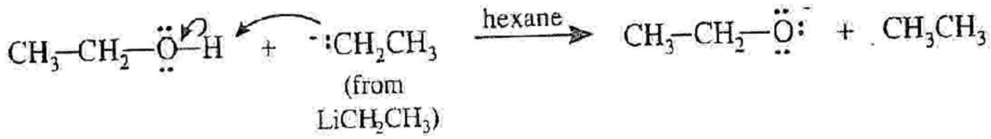


(c) No appreciable acid-base reaction takes place because CH_3CH_2ONa is too weak a base to remove a proton from ethyne.

(d)

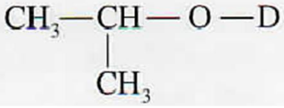


(e)



3.26 Aşağıdaki bileşiklerin sentezlerini uygun etiketsiz organik bileşiklerden çıkarak gösteriniz.

(a) $C_6H_5-C\equiv C-T$ (b)

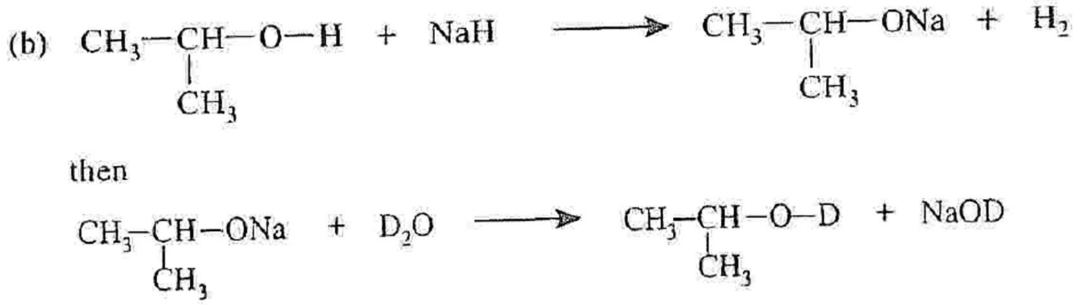


$CH_3-\underset{\displaystyle CH_3}{CH}-O-D$ (c) $CH_3CH_2CH_2OD$

3.26 (a) $C_6H_5-C\equiv C-H + NaNH_2 \xrightarrow{ether} C_6H_5-C\equiv C:^- Na^+ + NH_3$

then

$C_6H_5-C\equiv C:^- Na^+ + T_2O \longrightarrow C_6H_5-C\equiv C-T + NaOT$



(b) $CH_3-\underset{\displaystyle CH_3}{CH}-O-H + NaH \longrightarrow CH_3-\underset{\displaystyle CH_3}{CH}-ONa + H_2$

then

$CH_3-\underset{\displaystyle CH_3}{CH}-ONa + D_2O \longrightarrow CH_3-\underset{\displaystyle CH_3}{CH}-O-D + NaOD$

(c) $CH_3CH_2CH_2OH + NaH \longrightarrow CH_3CH_2CH_2ONa + H_2$

then

$CH_3CH_2CH_2ONa + D_2O \longrightarrow CH_3CH_2CH_2OD + NaOD$

3.27 **(a)** Aşağıdaki bileşikleri azalan asitliklerine göre sıralayınız ve cevabınızı açıklayınız: $CH_3CH_2NH_2$, CH_3CH_2OH ve $CH_3CH_2CH_3$. **(b)** a şıkkında verilen asitlerin konjuge bazlarını azalan bazlıklarına göre sıralayınız.

3.27 (a) $CH_3CH_2OH > CH_3CH_2NH_2 > CH_3CH_2CH_3$

Oxygen is more electronegative than nitrogen, which is more electronegative than carbon. The O-H bond is most polarized, the N-H bond is next, and the C-H bond is least polarized.

(b) $CH_3CH_2O^- < CH_3CH_2NH^- < CH_3CH_2CH_2^-$

The weaker the acid, the stronger the conjugate base.

3.28 Aşağıdaki bileşikleri azalan asitliklerine göre sıralayınız.

(a) $CH_3CH=CH_2$, $CH_3CH_2CH_3$, $CH_3C\equiv CH$

(b) $CH_3CH_2CH_2OH$, $CH_3CH_2CO_2H$, $CH_3CHClCO_2H$

(c) CH_3CH_2OH, $CH_3CH_2OH_2^+$, CH_3OCH_3

3.28 (a) $CH_3C\equiv CH > CH_3CH=CH_2 > CH_3CH_2CH_3$

(b) $CH_3CHClCO_2H > CH_3CH_2CO_2H > CH_3CH_2CH_2OH$

(c) $CH_3CH_2OH_2^+ > CH_3CH_2OH > CH_3OCH_3$

3.29 Aşağıdaki bileşikleri artan bazlıklarına göre sıralayınız.

(a) CH_3NH_2, $CH_3NH_3^+$, CH_3NH^-

(b) CH_3O^-, CH_3NH^-, $CH_3CH_2^-$

(c) $CHCH_3CH{=}CH^-$, $CH_3CH_2CH_2^-$, $CH_3C{\equiv}C^-$

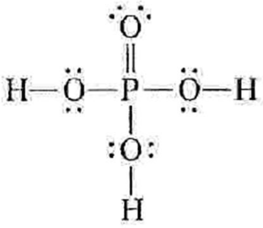
3.29 (a) $CH_3NH_3^+ < CH_3NH_2 < CH_3NH^-$

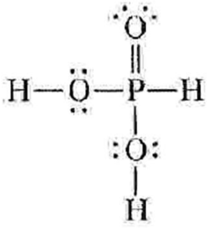
(b) $CH_3O^- < CH_3NH^- < CH_3CH_2^-$

(c) $CH_3C{\equiv}C^- < CH_3CH{=}CH^- < CH_3CH_2CH_2^-$

3.30 H_3PO_4 bir triprotik asit iken H_3PO_3 bir diprotik asittir. Bu iki asit için davranışlarındaki farkı açıklayan yapılarını çiziniz.

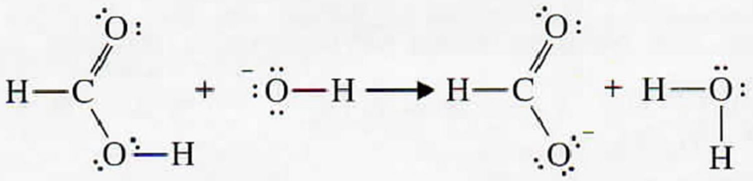
3.30 The acidic hydrogens must be attached to oxygen atoms. In H_3PO_3, one hydrogen is bonded to a phosphorus atom:



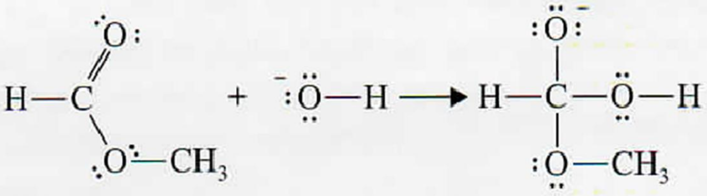


3.31 Aşağıdaki tepkimelerde gerekli eğri okları çiziniz.

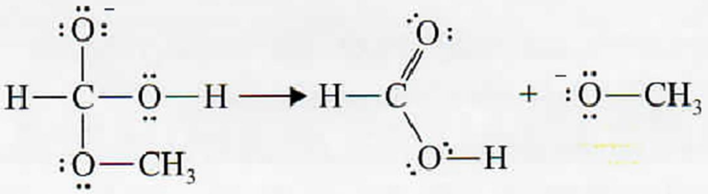
(a)



(b)

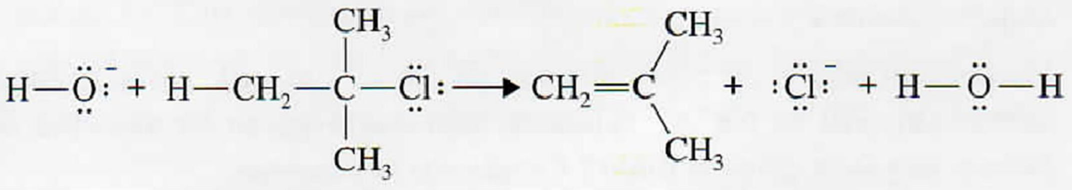


(c)

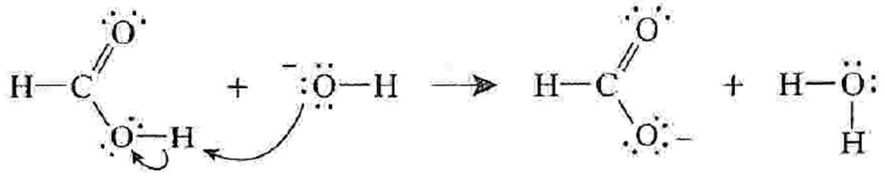


(d) $H-\ddot{\underset{..}{O}}:^- + CH_3-\ddot{\underset{..}{I}}: \longrightarrow H-\ddot{\underset{..}{O}}-CH_3 + :\ddot{\underset{..}{I}}:^-$

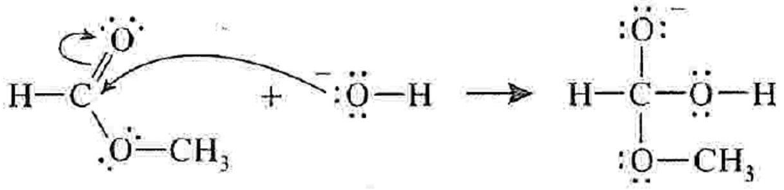
(e)



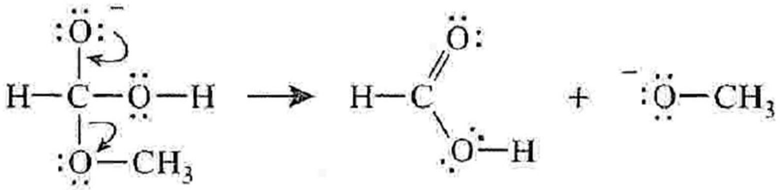
3.31 (a)



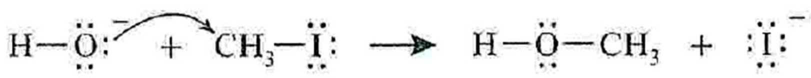
(b)



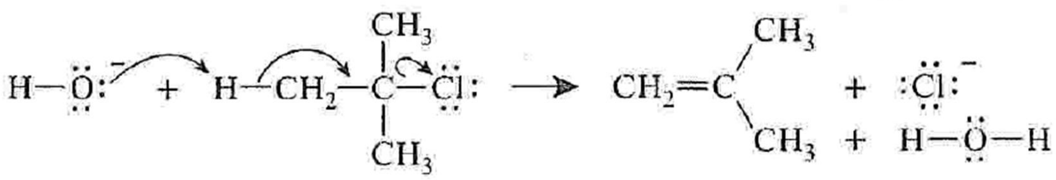
(c)



(d)



(e)

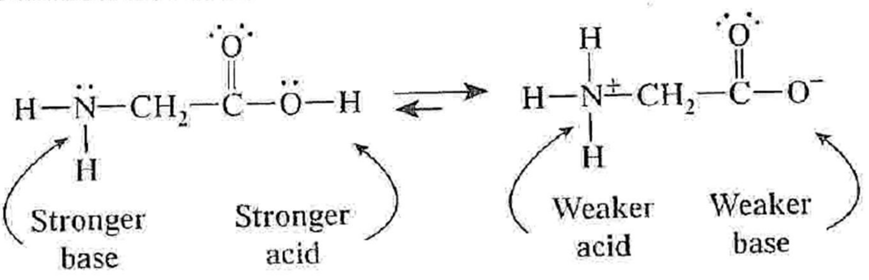


3.32 Glisin pek çok proteinden elde edilebilen bir amino asittir. Glisin, çözeltide iki yapının dengesi halinde bulunur.

$$H_2NCH_2CO_2H \rightleftharpoons H_3\overset{+}{N}CH_2CO_2^-$$

(a) Çizelge 3.1'den yararlanarak dengede hangi şeklin tercih edildiğini belirtiniz. **(b)** Glisinin erime noktasının 262°C (bozunuyor) olduğunu el kitabından öğreniyoruz. Hangi yapı glisini daha iyi temsil ediyor?

3.32 (a) Assume that the acidic and basic groups of glycine in its two forms have acidities and basicities similar to those of acetic acid and methylamine. Then consider the equilibrium between the two forms:



We see that the ionic form contains the groups that are the weaker acid and weaker base. The equilibrium, therefore, will favor this form.

(b) The high melting point shows that the ionic structure better represents glycine.

3.33 Malonik asit , $HO_2CCH_2CO_2H$, bir diprotik asittir. Birinci protonun kaybı için olan pK_a 2,83 ; ikinci proton kaybı için olan pK_a 5,69'dur. **(a)** malonik asitin asetik asitten (pK_a=4,75) niçin daha kuvvetli olduğunu açıklayınız. **(b)** $^-O_2CCH_2CO_2H$ anyonunun niçin malonik asitin kendisinden çok daha zayıf asit olduğunu açıklayınız.

3.33 (a) The second carboxyl group of malonic acid acts as an electron-withdrawing group and stabilizes the conjugate base formed (i.e., $HO_2CCH_2CO_2^-$) when malonic acid loses a proton. [Any factor that stabilizes the conjugate base of an acid always increases the strength of the acid (Section 3.10C).] An important factor here may be an entropy effect as explained in Section 3.9.

(b) When $^-O_2CCH_2CO_2H$ loses a proton, it forms a dianion, $^-O_2CCH_2CO_2^-$. This dianion is destabilized by having two negative charges in close proximity.

3.34 HA asidinin iyonlaşması için serbest enerji değişimi, 21 kj mol^{-1}; HB asidi için −21 kj mol^{-1}'dir. Hangisi daha kuvvetli asittir?

3.34 HB is the stronger acid.

3.35 25°C'da trikloroasetik asitin iyonlaşması için entalpi değişimi, $\Delta H°$, +6,3 kJ mol^{-1} ve entropi değişimi , $\Delta S°$, +0,0084 kj mol^{-1} K^{-1}'dir. Trikloroasetik asitin pK_a'sı nedir?

3.35
$$\begin{aligned}\Delta G° &= \Delta H° - T\Delta S° \\ &= 6.3 \text{ kJ mol}^{-1} - (298 \text{ K})(0.0084 \text{ kJ mol}^{-1}\text{K}^{-1}) \\ &= 3.8 \text{ kJ mol}^{-1}\end{aligned}$$

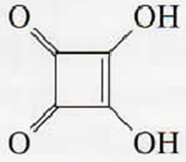
$$\log K_{eq} = \log K_a = -\text{p}K_a = -\frac{\Delta G°}{2.303RT}$$

$$\text{p}K_a = \frac{\Delta G°}{2.303RT}$$

$$\text{p}K_a = \frac{3.8 \text{ kJ mol}^{-1}}{(2.303)(0.008314 \text{ kJ mol}^{-1}\text{K}^{-1})(298 \text{ K})}$$

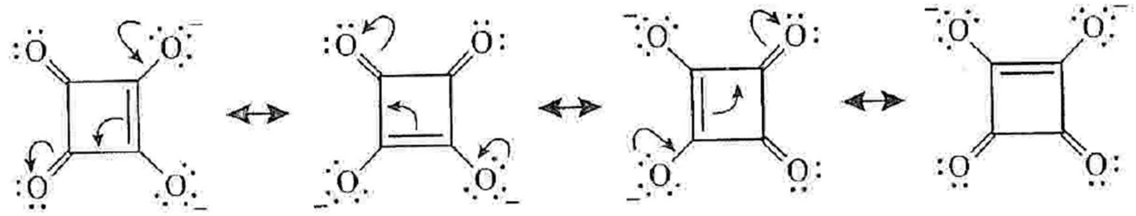
$$\text{p}K_a = 0.66$$

3.36 Aşağıdaki bileşiğe **skuarik asit** adı verilmiştir (İng. square: kare). Skuarik asit bir diprotik asittir, her iki proton da asetik asitten daha asidiktir. İki protonun kaybedilmesinden sonra oluşan dianyonda tüm karbon–karbon bağları aynı uzunlukta olduğu gibi karbon–oksijen bağları da tam olarak öyledir. Bu gözlemler için bir rezonans açıklama yapınız.



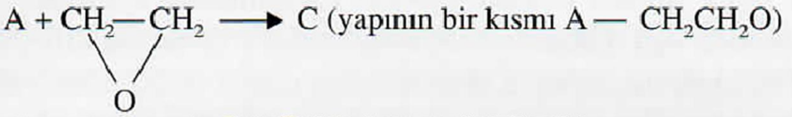
Skuarik asit

3.36 The dianion is a hybrid of the following resonance structures:



If we mentally fashion a hybrid of these structures, we see that each carbon-carbon bond is a single bond in three structures and a double bond in one. Each carbon-oxygen bond is a double bond in two structures and a single bond in two structures. Therefore, we would expect all of the carbon-carbon bonds to be equivalent and of the same length, and exactly the same can be said for the carbon-oxygen bonds.

***3.37** $CH_3CH_2SH + CH_3O^- \longrightarrow$ A (kükürt içeriyor) + B



$A + CH_2—CH_2$ (O) $\longrightarrow$ C (yapının bir kısmı A— CH_2CH_2O)

$C + H_2O \longrightarrow$ D + E (bir inorganik bileşik)

(a) Yukarıda verilen tepkime serisinde A'dan E'ye kadar olan yapıları yazınız.

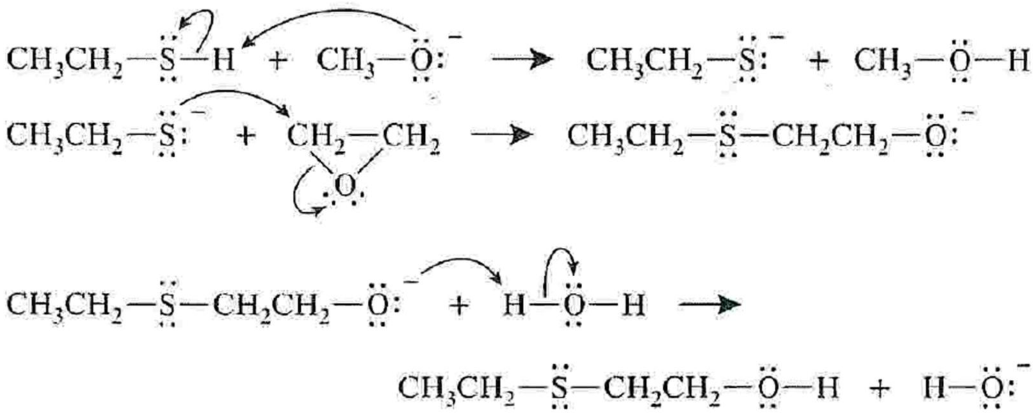
(b) Tepkime serisini eğri oklarla ve tüm ortaklaşılmamış elektron çiftlerini göstererek yeniden yazınız.

*3.37 (a) *A* is $CH_3CH_2S^-$ *B* is CH_3OH

C is $CH_3CH_2SCH_2CH_2O^-$ *D* is $CH_3CH_2SCH_2CH_2OH$

E is OH^-

(b)



$CH_3CH_2—S—H + CH_3—O:^- \longrightarrow CH_3CH_2—S:^- + CH_3—O—H$

$CH_3CH_2—S:^- + CH_2—CH_2$ (O) $\longrightarrow CH_3CH_2—S—CH_2CH_2—O:^-$

$CH_3CH_2—S—CH_2CH_2—O:^- + H—O—H \longrightarrow$

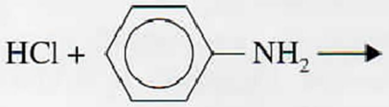
$CH_3CH_2—S—CH_2CH_2—O—H + H—O:^-$

***3.38** Önce aşağıdaki eşitliklerin her birini tamamlayınız ve denkleştiriniz. Bu tepkimeler için etanol , heksan ve sıvı amonyak arasından uygun olabilecek çözücüyü (birden fazla da olabilir) belirtiniz. "Benzer benzeri çözer" ilkesinin pratikte getirdiği sınırlamaları gözardı ederek cevaplarınızı sadece bağıl asitliklere dayandırınız.

(a) $CH_3(CH_2)_8OD + CH_3(CH_2)_8Li \longrightarrow$

(b) $NaNH_2 + CH_3C{\equiv}CH \longrightarrow$

(c)



HCl + C_6H_5—$NH_2 \longrightarrow$

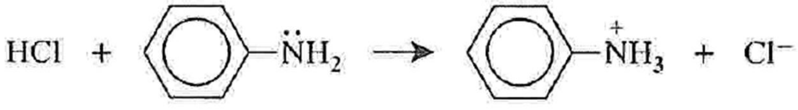
(Bu aminin , anilin, konjuge asidinin pK_a'sı 4.6'dır.)

*3.38 (a) $CH_3(CH_2)_8OD + CH_3(CH_2)_8\,Li \longrightarrow CH_3(CH_2)_8O^- \, Li^+ + CH_3(CH_2)_8D$

Hexane could be used as solvent. Liquid ammonia and ethanol could not because they would compete with $CH_3(CH_2)_8OD$ and generate mostly non-deuterio-labelled $CH_3(CH_2)_7CH_3$.

(b) $NH_2^- + CH_3C{\equiv}CH \longrightarrow NH_3 + CH_3C{\equiv}C{:}^-$

Hexane or liquid ammonia could be used: ethanol is too acidic and would lead to $CH_3CH_2O^-$ (ethoxide ion) instead of the desired alkynide ion.

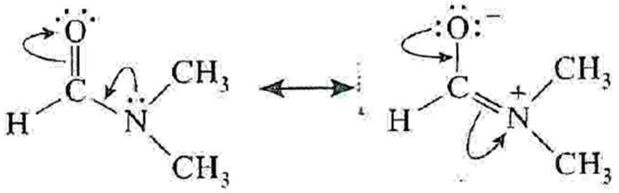
(c) 

Hexane or ethanol could be used; liquid ammonia is too strong a base and would lead to NH_4^+ instead of the desired anilinium ion.

***3.39** Dimetilformamit (DMF), $HCON(CH_3)_2$, bir polar aprotik çözücü örneğidir; aprotik , onun oldukça elektronegatif bir atoma bağlı hidrojeni olmadığı anlamına gelir. **(a)** Ortaklaşılmamış elektron çiftlerini göstererek çizgi bağ yapı formüllerini çiziniz. **(b)** Öngördüğünüz en önemli rezonans yapılarını (biri a için verdiğiniz cevap) çiziniz. **(c)** DMF , çözücü olarak kullanıldığında aşağıdaki gibi tepkimelerde nükleofillerin (örn. sodyum siyanürden gelen CN^-) tepkimeye yatkınlığını aşırı derecede arttırır:

$$NaCN + CH_3CH_2Br \longrightarrow CH_3CH_2C{\equiv}N + NaBr$$

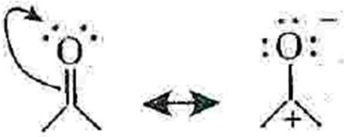
DMF'nin bu etkisini Lewis asit–baz tartışmaları ışığında açıklayınız. (İpucu: Su ve alkoller anyonlar ve katyonları sararken DMF, sadece katyonları sarmakta etkindir.)

*3.39 (a,b) 

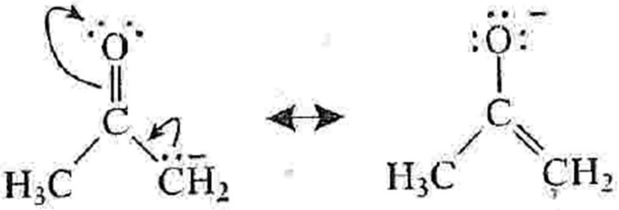
(c) Since DMF does not bind with (solvate) anions, their electron density remains high and their size small, both of which make nucleophiles more reactive.

***3.40** Çizelge 3.1 de verildiği gibi asetonun CH_3COCH_3 , pK_a'sı 19,2 dir. **(a)** Aseton ve varsa katkısı olan diğer rezonans yapılarının çizgi – bağ formüllerini çiziniz. **(b)** Asetonun konjuge bazının ve varsa katkısı olan diğer rezonans yapılarını öngörünüz ve çiziniz. **(c)** CH_3COCH_2D'yi sentezlemek için kullanılabilecek olan bir tepkimenin denklemini yazınız.

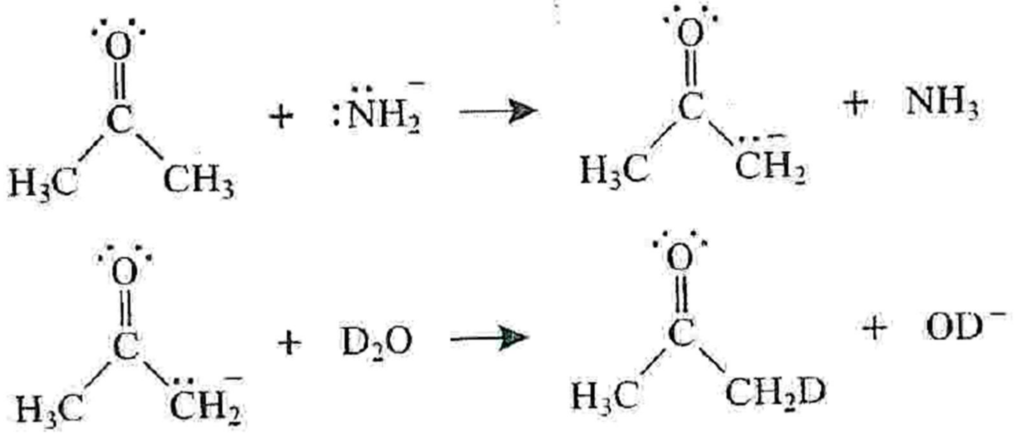
3.40 (a)



(b)



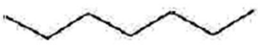
(c)



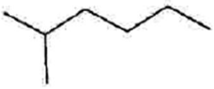
Alkanlar: Adlandırma, Konformasyon Analizi ve Sentezlere Giriş

Problem 4.1 ➤ C_7H_{16} molekül formülüne sahip tüm yapı izomerlerinin yapı formüllerini yazınız. (Toplam 9 yapı izomeri vardır.)

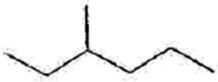
4.1



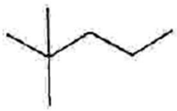
Heptane



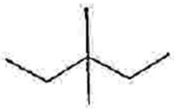
2-Methylhexane



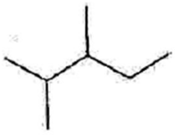
3-Methylhexane



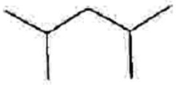
2,2-Dimethylpentane



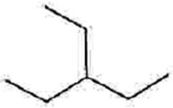
3,3-Dimethylpentane



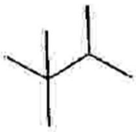
2,3-Dimethylpentane



2,4-Dimethylpentane



3-Ethylpentane

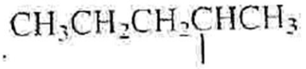


2,2,3-Trimethylbutane

Problem 4.2 ➤ Biraz önce verilen 2,2-dimetilpropile (veya neopentile) ek olarak yedi tane beş karbonlu grup daha vardır. Bunların yapılarını ve her birinin sistematik adını yazınız. b) Problem 4.1'de cevap olarak verdiğiniz C_7H_{16}'nın dokuz izomerinin de IUPAC adlarını yazınız.

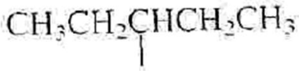
4.2 (a) $CH_3CH_2CH_2CH_2CH_2—$

Pentyl



$CH_3CH_2CH_2\underset{|}{C}HCH_3$

1-Methylbutyl



$CH_3CH_2\underset{|}{C}HCH_2CH_3$

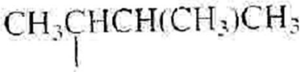
1-Ethylpropyl

$CH_3CH_2CH(CH_3)CH_2—$

2-Methylbutyl

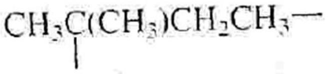
$CH_3CH(CH_3)CH_2CH_2—$

3-Methylbutyl



$CH_3\underset{|}{C}HCH(CH_3)CH_3$

1,2-Dimethylpropyl



$CH_3\underset{|}{C}(CH_3)CH_2CH_3—$

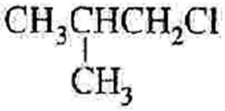
1,1-Dimethylpropyl

(b) See the answer to Problem 4.1 for the names of C_7H_{16} isomers.

a) C_4H_9Cl ve b) $C_5H_{11}Br$'nin tüm izomerlerinin IUPAC adlarını yazınız ◄ **Problem 4.3**

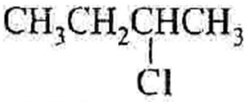
4.3 (a) $CH_3CH_2CH_2CH_2Cl$

1-Chlorobutane



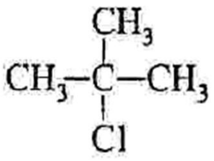
$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2Cl$

1-Chloro-2-methylpropane



$CH_3CH_2\underset{Cl}{\underset{|}{C}}HCH_3$

2-Chlorobutane

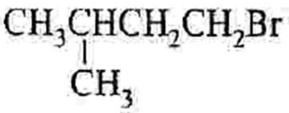


$CH_3-\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_3$

2-Chloro-2-methylpropane

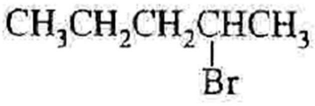
(b) $CH_3CH_2CH_2CH_2CH_2Br$

1-Bromopentane



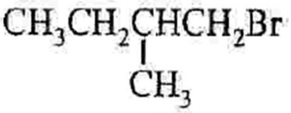
$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2Br$

1-Bromo-3-methylbutane



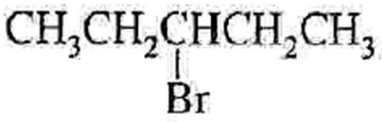
$CH_3CH_2CH_2\underset{Br}{\underset{|}{C}}HCH_3$

2-Bromopentane

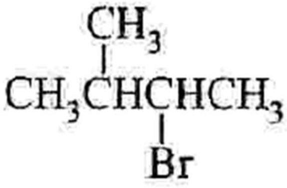


$CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCH_2Br$

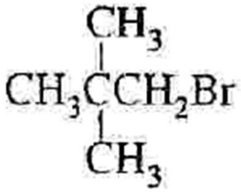
1-Bromo-2-methylbutane


$CH_3CH_2\underset{\displaystyle Br}{CH}CH_2CH_3$

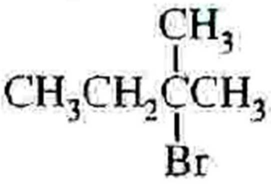
3-Bromopentane


$CH_3\overset{\displaystyle CH_3}{CH}\underset{\displaystyle Br}{CH}CH_3$

2-Bromo-3-methylbutane


$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_2Br$

1-Bromo-2,2-dimethylpropane

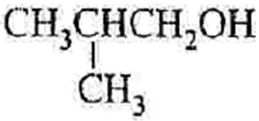

$CH_3CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}CH_3$

2-Bromo-2-methylbutane

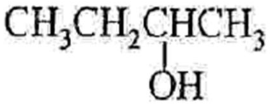
Problem 4.4 ➤ a) $C_4H_{10}O$ ve b) $C_5H_{12}O$ formüllerine sahip tüm izomer alkollerin IUPAC sistematik adlarını yazınız.

4.4 (a) $CH_3CH_2CH_2CH_2OH$

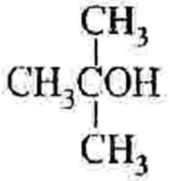
1-Butanol


$CH_3\underset{\displaystyle CH_3}{CH}CH_2OH$

2-Methyl-1-propanol


$CH_3CH_2\underset{\displaystyle OH}{CH}CH_3$

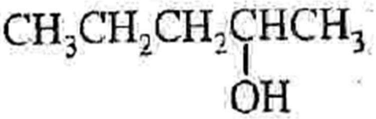
2-Butanol


$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}OH$

2-Methyl-2-propanol

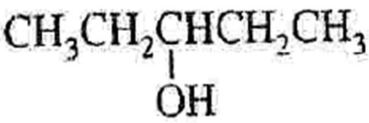
(b) $CH_3CH_2CH_2CH_2CH_2OH$

1-Pentanol



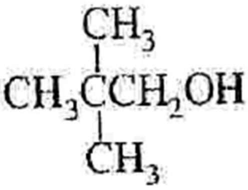
$CH_3CH_2CH_2\underset{\substack{|\\OH}}{C}HCH_3$

2-Pentanol



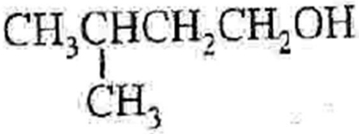
$CH_3CH_2\underset{\substack{|\\OH}}{C}HCH_2CH_3$

3-Pentanol



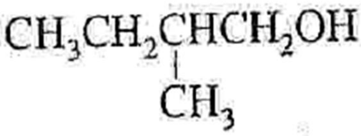
$CH_3\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}CH_2OH$

2,2-Dimethyl-1-propanol



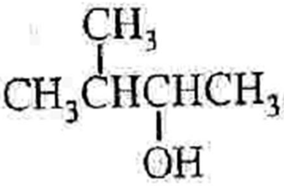
$CH_3\underset{\substack{|\\CH_3}}{C}HCH_2CH_2OH$

3-Methyl-1-butanol



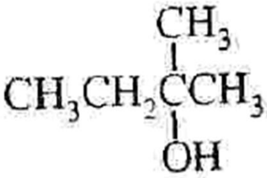
$CH_3CH_2\underset{\substack{|\\CH_3}}{C}HCH_2OH$

2-Methyl-1-butanol



$CH_3\overset{\substack{CH_3\\|}}{C}H\underset{\substack{|\\OH}}{C}HCH_3$

3-Methyl-2-butanol



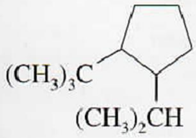
$CH_3CH_2\overset{\substack{CH_3\\|}}{\underset{\substack{|\\OH}}{C}}CH_3$

2-Methyl-2-butanol

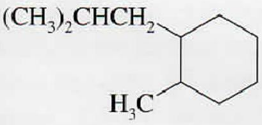
Problem 4.5

Aşağıdaki sübstitüe alkanları adlandırınız.

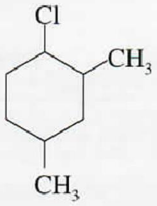
(a)



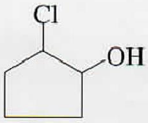
(b)



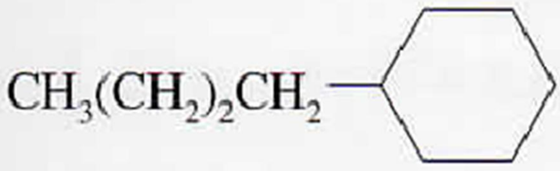
(d)



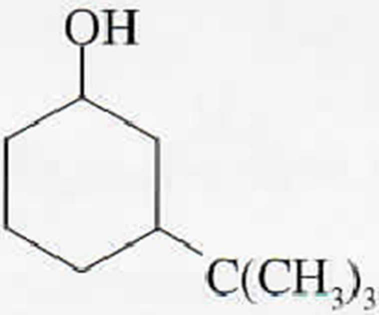
(e)



(c)



(f)



4.5 (a) 1-(1-Methylethyl)-2-(1,1-dimethylethyl)cyclopentane or 1-*tert*-butyl-2-isopropylcyclopentane

(b) 1-Methyl-2-(2-methylpropyl)cyclohexane or 1-isobutyl-2-methylcyclohexane

(c) Butylcyclohexane

(d) 1-Chloro-2,4-dimethylcyclohexane

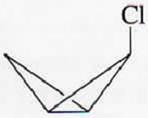
(e) 2-Chlorocyclopentanol

(f) 3-(1,1-Dimethylethyl)cyclohexanol or 3-*tert*-butylcyclohexanol

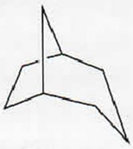
---

Problem 4.6 ➤ Aşağıdaki bisiklik alkanların her birini adlandırınız.

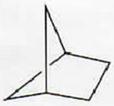
(a)



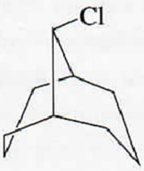
(b)



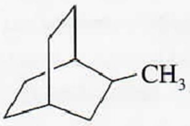
(c)



(d)



(e)



(f) Bisiklo[2.2.0]heksanın izomeri olan bir bisiklik bileşiğin yapısını yazınız ve adlandırınız.

4.6 (a) 2-Chlorobicyclo[1.1.0]butane

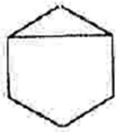
(b) Bicyclo[3.2.1]octane

(c) Bicyclo[2.1.1]hexane

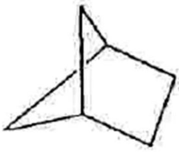
(d) 9-Chlorobicyclo[3.3.1]nonane

(e) 2-Methylbicyclo[2.2.2]octane

(f)



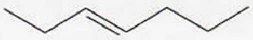
Bicyclo[3.1.0]hexane or



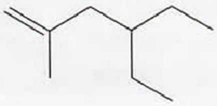
bicyclo[2.1.1]hexane

Problem 4.7 ➤ Aşağıdaki alkenleri IUPAC'a göre adlandırınız.

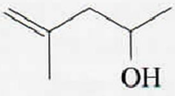
(a)



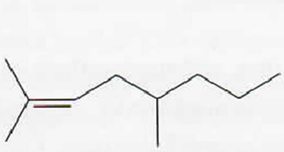
(c)



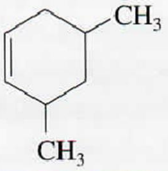
(e)



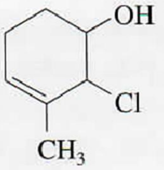
(b)



(d)



(f)



4.7 (a) *trans*-3-Heptene

(b) 2,5-Dimethyl-2-octene

(c) 4-Ethyl-2-methyl-1-hexene

(d) 3,5-Dimethylcyclohexene

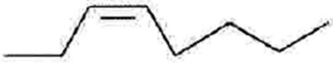
(e) 4-Methyl-4-penten-2-ol

(f) 2-Chloro-3-methyl-3-cyclohexen-1-ol

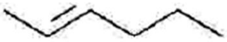
Problem 4.8 ➤ Aşağıdaki bileşiklerin yapı formüllerini yazınız.

- **(a)** *cis*-3-Okten
- **(b)** *trans*-2-Heksen
- **(c)** 2,4-Dimetil-2-penten
- **(d)** *trans*-1-Kloro-2-büten
- **(e)** 4,5-Dibromo-1-penten
- **(f)** 1,3-Dimetilsikloheksen
- **(g)** 3,4-Dimetilsiklopenten
- **(h)** Vinilsiklopentan
- **(i)** 1,2-Diklorosikloheksen
- **(j)** *trans*-1,4-dikloro-2-penten

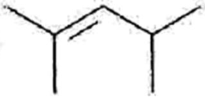
4.8 (a)



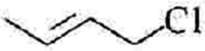
(b)



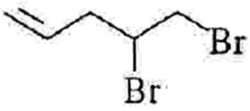
(c)



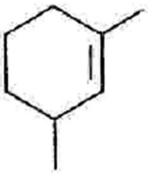
(d)



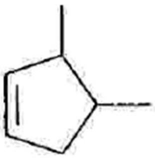
(e)



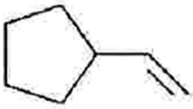
(f)



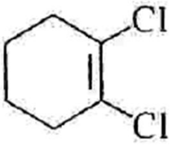
(g)



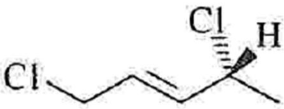
(h)



(i)

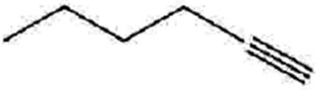


(j)

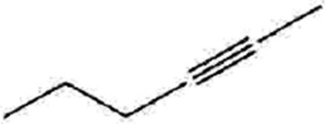


C_6H_{10} formülüne sahip tüm alkinlerin yapılarını ve IUPAC adlarını yazınız. ◀ **Problem 4.9**

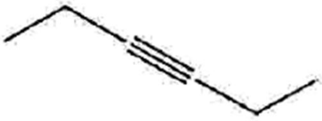
4.9



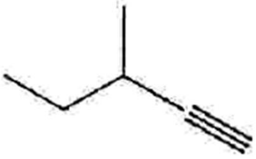
1-Hexyne



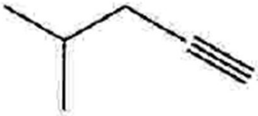
2-Hexyne



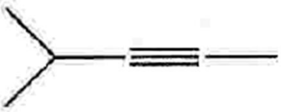
3-Hexyne



3-Methyl-1-pentyne



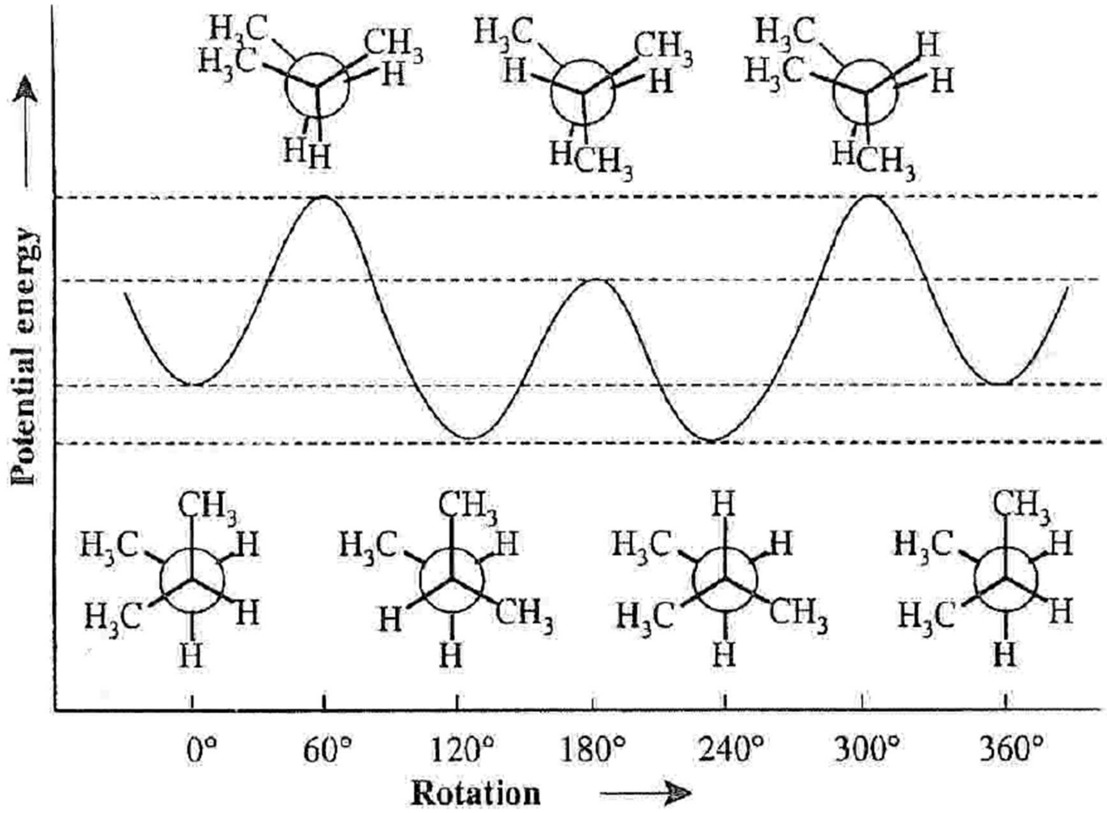
4-Methyl-1-pentyne



4-Methyl-2-pentyne

2-Metilbütanın C2–C3 bağındaki dönmeden kaynaklanan enerji değişimlerini gösteren, Şekil 4.8'dekine benzer bir eğri çiziniz. Enerji değişimlerinin gerçek sayısal değerleri ile ilgilenmeniz gerekmez, ancak tüm maksimum ve minimumlara karşılık gelen uygun konformasyonları yazınız. ◀ **Problem 4.10**

4.10



Metilsikloheksanın 25°C'da aksiyal ve ekvatoryal şekilleri arasındaki 7,6 kJ mol^{-1}'lik serbest enerji farkının (ekvatoryal olanı daha kararlı) % 95 ekvatoryal yapı içeren denge karışımı ile uyum içerisinde olduğunu hesaplayarak gösteriniz. ($\Delta G° = -2{,}303\ RT \log k_{denge}$ eşitliğini kullanın). ◄ **Problem 4.11**

4.11

$$\log K_{eq} = \frac{\Delta G°}{-2.303RT} = \frac{-7600\ \mathrm{J}}{(-2.303)(8.314\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})} = 1.32$$

$$K_{eq} = 21.38$$

Let e = amount of equatorial form

and a = amount of axial form

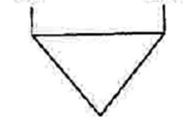
$$\text{then, } K_{eq} = \frac{e}{a} = 21.38$$

$$e = 21.38a$$

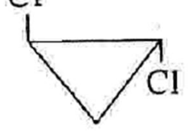
$$\%e = \frac{21.38a}{a + 21.38a} \times 100 = 95.5\%$$

Problem 4.12 ➤ (a) 1,2-Dimetilsiklopropanın ve (b) 1,3-Dibromosiklobütanın cis ve trans izomerlerinin yapılarını yazınız.

4.12 (a)

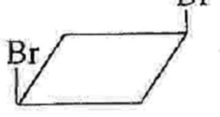


(cis)

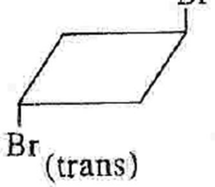


(trans)

(b)



(cis)

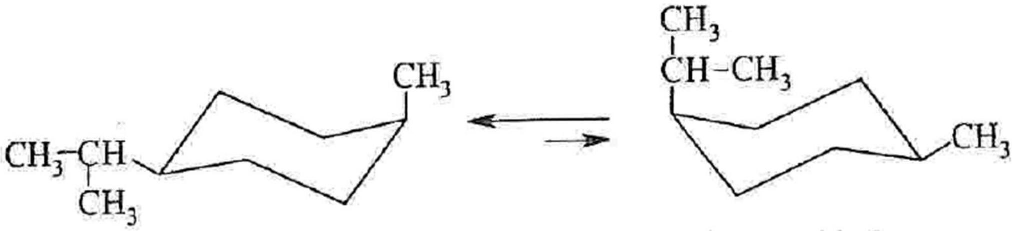


(trans)

Problem 4.13

(a) *cis*-1-İzopropil-4-metilsikloheksanın iki sandalye konformasyonunun yapı formüllerini yazınız. (b) Bu iki konformasyon eşdeğer midir? (c) Değilse hangisi daha kararlıdır? (d) Dengede yeğlenen konformasyon hangisi olmalıdır?

4.13 (a-d)



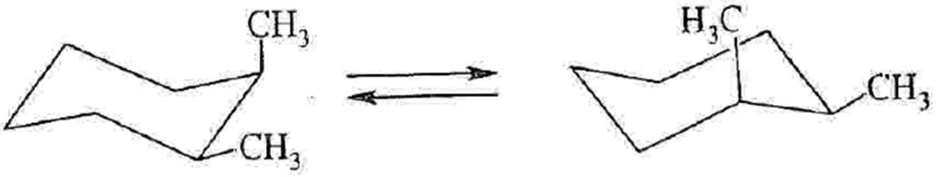
More stable because larger group is equatorial

Less stable because larger group is axial

Problem 4.14

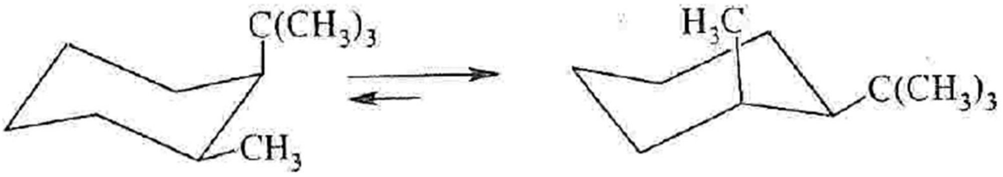
(a) *cis*-1,2-Dimetilsikloheksanın iki konformasyonunu yazınız. (b) Bu iki konformasyon eş potansiyel enerjili olabilir mi? (c) *cis*-1-*ter*-Bütil-2-metilsikloheksanın iki konformasyonundaki durum nedir? (d) trans-1,2-Dimetilsikloheksanın iki konformasyonu aynı potansiyel enerjili olabilir mi?

4.14 (a)



(b) Yes

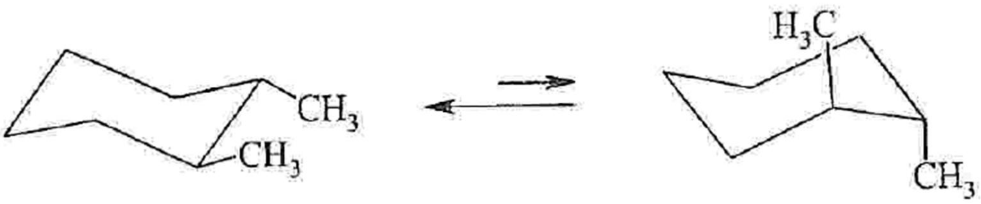
(c)



Less stable because the large *tert*-butyl group is axial

More stable because the large *tert*-butyl group is equatorial

(d)



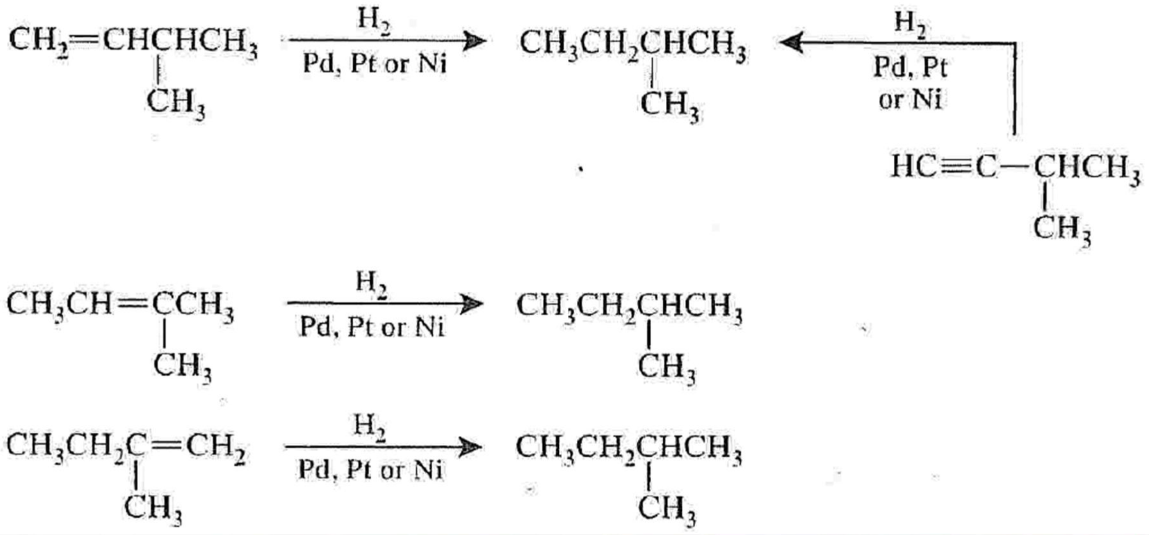
More stable because both methyl groups are equatorial

Less stable because both methyl groups are axial

Problem 4.15

Hidrojenlendiğinde 2-metilbütan verebilecek alken ve alkinleri yazınız.

4.15



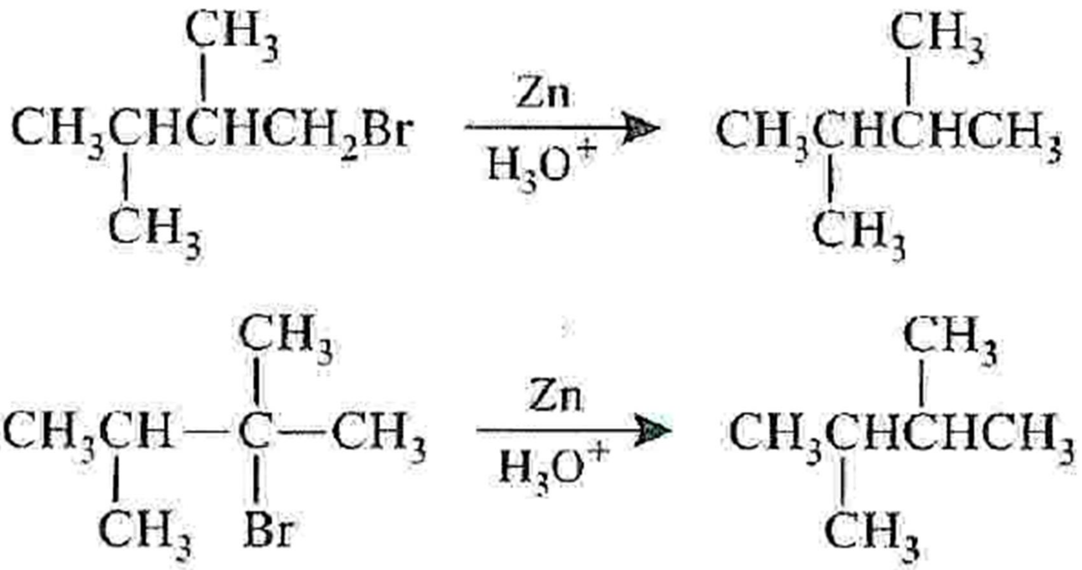
$$CH_2{=}CH\underset{\substack{|\\ CH_3}}{C}HCH_3 \xrightarrow[\text{Pd, Pt or Ni}]{H_2} CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HCH_3 \xleftarrow[\text{Pd, Pt or Ni}]{H_2} HC{\equiv}C{-}\underset{\substack{|\\ CH_3}}{C}HCH_3$$

$$CH_3CH{=}\underset{\substack{|\\ CH_3}}{C}CH_3 \xrightarrow[\text{Pd, Pt or Ni}]{H_2} CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HCH_3$$

$$CH_3CH_2\underset{\substack{|\\ CH_3}}{C}{=}CH_2 \xrightarrow[\text{Pd, Pt or Ni}]{H_2} CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HCH_3$$

Problem 4.16 ➤ Hedefiniz bir alkil halojenürü, çinko ve sulu asit ile etkileştirerek 2,3-dimetilbütanı elde etmek olsun. Bunu yapmak için iki yöntem (farklı iki alkil halojenüründen çıkarak) gösteriniz.

4.16

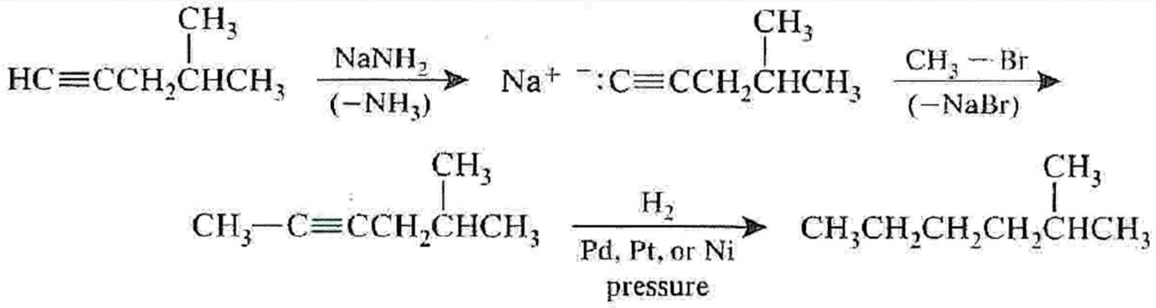


$$CH_3\underset{\substack{|\\ CH_3}}{C}H\overset{\substack{CH_3\\ |}}{C}HCH_2Br \xrightarrow[H_3O^+]{Zn} CH_3\underset{\substack{|\\ CH_3}}{C}H\overset{\substack{CH_3\\ |}}{C}HCH_3$$

$$CH_3\underset{\substack{|\\ CH_3}}{C}H{-}\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ Br}}{C}}{-}CH_3 \xrightarrow[H_3O^+]{Zn} CH_3\underset{\substack{|\\ CH_3}}{C}H\overset{\substack{CH_3\\ |}}{C}HCH_3$$

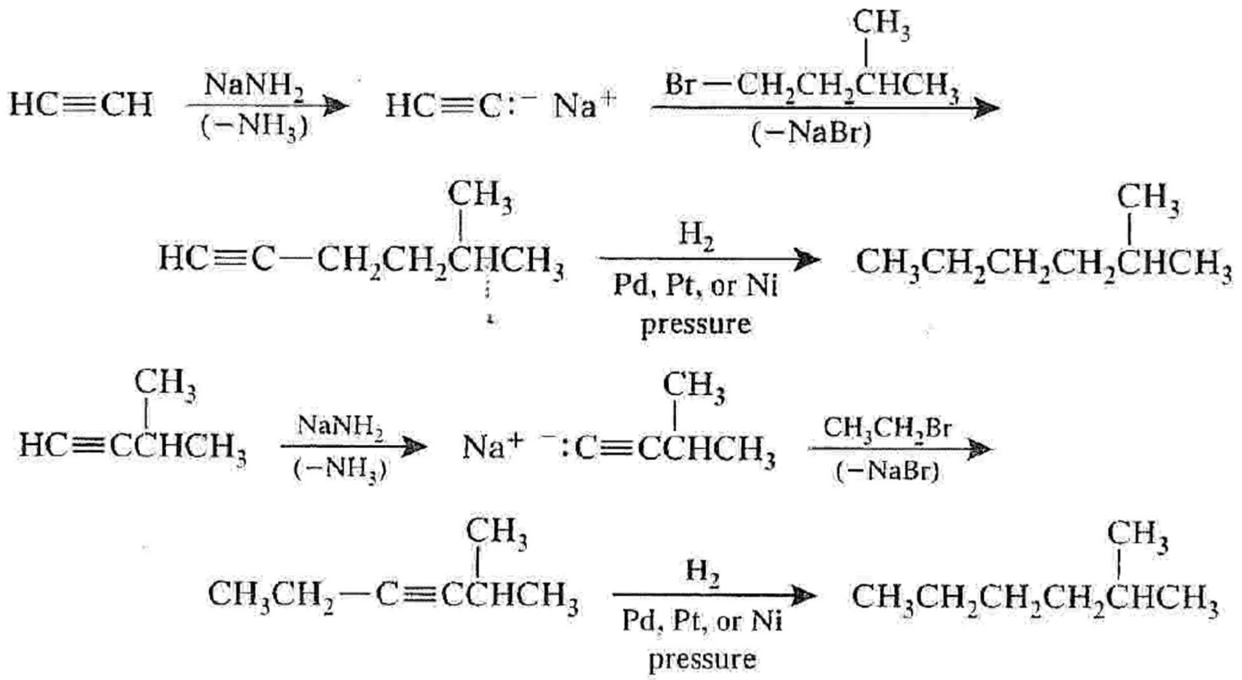
Problem 4.17 ➤ Bu kısımda verilen 2-metilheksanın retrosentetik analizine bakarak uygun olan sentetik süreç için tepkimeleri yazınız.

4.17



$$HC{\equiv}CCH_2\overset{\substack{CH_3\\ |}}{C}HCH_3 \xrightarrow[(-NH_3)]{NaNH_2} Na^+\ {}^-{:}C{\equiv}CCH_2\overset{\substack{CH_3\\ |}}{C}HCH_3 \xrightarrow[(-NaBr)]{CH_3-Br}$$

$$CH_3{-}C{\equiv}CCH_2\overset{\substack{CH_3\\ |}}{C}HCH_3 \xrightarrow[\substack{\text{Pd, Pt, or Ni}\\ \text{pressure}}]{H_2} CH_3CH_2CH_2CH_2\overset{\substack{CH_3\\ |}}{C}HCH_3$$



$$HC{\equiv}CH \xrightarrow[(-NH_3)]{NaNH_2} HC{\equiv}C:^- \; Na^+ \xrightarrow[(-NaBr)]{Br-CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3}$$

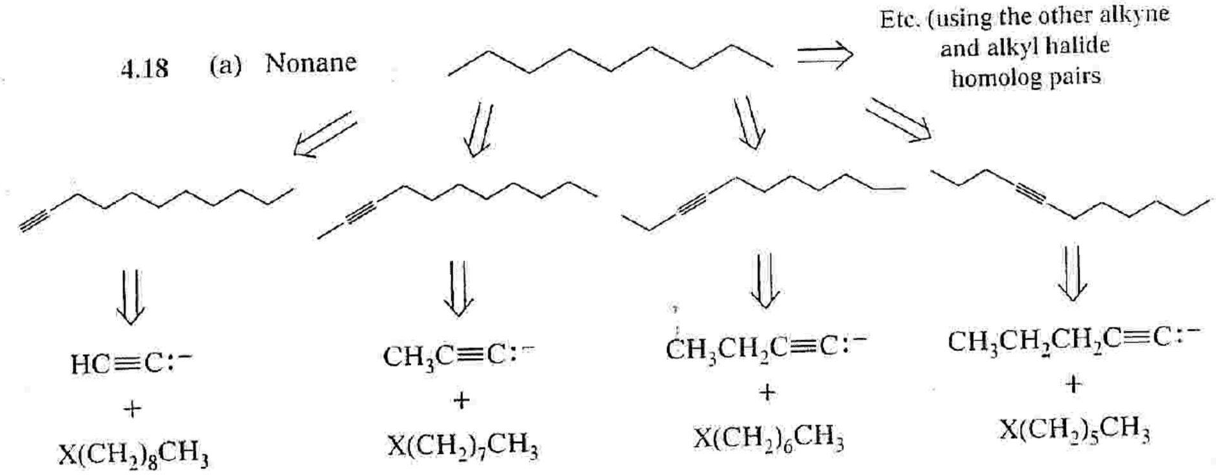
$$HC{\equiv}C-CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3 \xrightarrow[\text{Pd, Pt, or Ni pressure}]{H_2} CH_3CH_2CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$$

$$HC{\equiv}C\overset{CH_3}{\overset{|}{C}}HCH_3 \xrightarrow[(-NH_3)]{NaNH_2} Na^+ \; ^-{:}C{\equiv}C\overset{CH_3}{\overset{|}{C}}HCH_3 \xrightarrow[(-NaBr)]{CH_3CH_2Br}$$

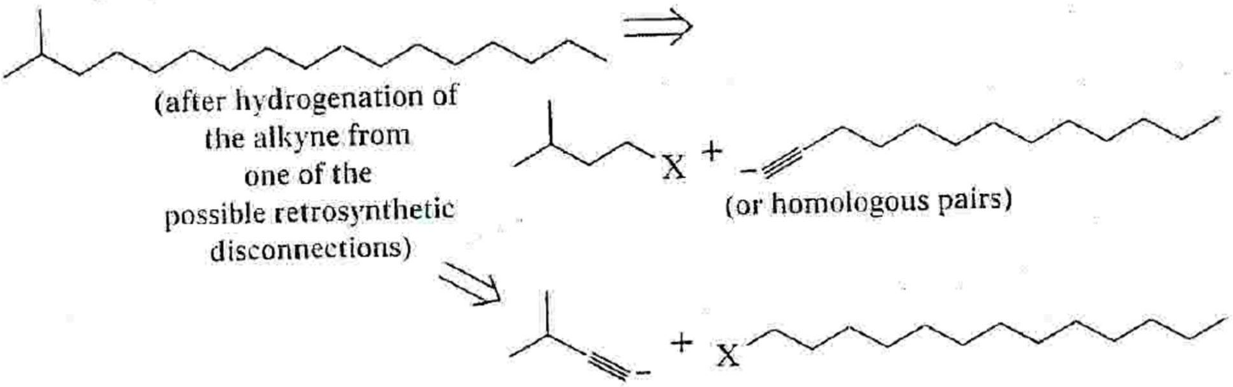
$$CH_3CH_2-C{\equiv}C\overset{CH_3}{\overset{|}{C}}HCH_3 \xrightarrow[\text{Pd, Pt, or Ni pressure}]{H_2} CH_3CH_2CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$$

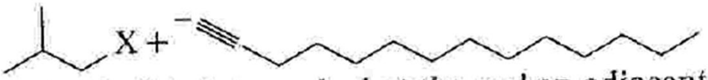
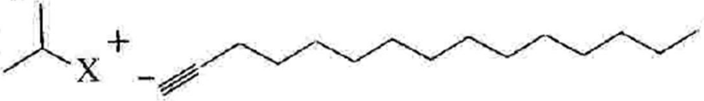
Problem 4.18 ➤ **(a)** Böcek feromonları olan undekan ve 2-metilheptadekan (Altbölüm 4.16) için, alkinür iyonunun alkillenmesiyle yapılan sentezden yararlanarak tüm retrosentetetik süreci yazınız (Altbölüm 4.16).

4.18 (a) Nonane

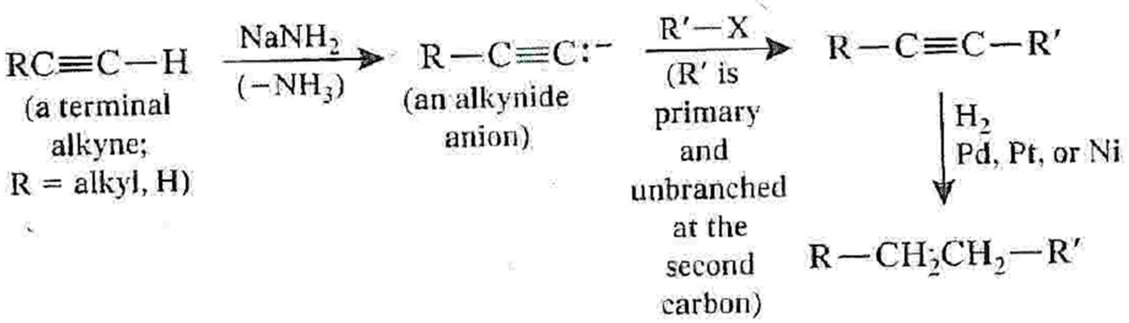


2-Methylheptadecane


(after hydrogenation of the alkyne from one of the possible retrosynthetic disconnections)
X
+
(or homologous pairs)
+
X

(Note that  is not a good choice because the alkyl halide is branched at the carbon adjacent to the halogen. Neither would  work because the alkyl halide is secondary.)

(b) For any pair of reactants above that is a feasible retrosynthetic disconnection, the steps for the synthesis would be



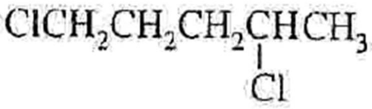
$$RC{\equiv}C{-}H \xrightarrow[(-NH_3)]{NaNH_2} R{-}C{\equiv}C{:}^{-} \xrightarrow[\text{(R}' \text{ is primary and unbranched at the second carbon)}]{R'{-}X} R{-}C{\equiv}C{-}R' \xrightarrow[\text{Pd, Pt, or Ni}]{H_2} R{-}CH_2CH_2{-}R'$$

(a terminal alkyne; R = alkyl, H)

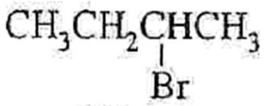
(an alkynide anion)

4.19 Aşağıdakilerin her birinin yapı formülünü yazınız .

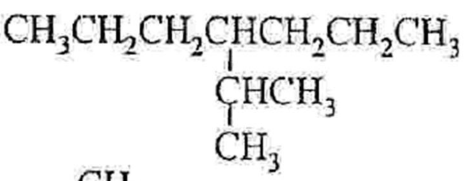
(a) 1,4-Dikloropentan
(b) *sek*-Bütil bromür
(c) 4-İzopropilheptan
(d) 2,2,3-Trimetilpentan
(e) 3-Etil-2-metilheksan
(f) 1,1-Diklorosiklopentan
(g) *cis*-1,2-Dimetilsiklopropan
(h) *trans*-1,2-Dimetilsiklopropan
(i) 4-Metil-2-pentanol
(j) *trans*-4-İzobütilsikloheksanol
(k) 1,4-Disiklopropilheksan
(l) Neopentil alkol
(m) Bisiklo[2,2,2]oktan
(n) Bisiklo[3,1,1]heptan
(o) Siklopentilsiklopentan

4.19 (a) 

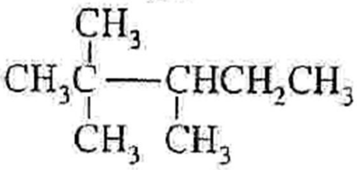
$ClCH_2CH_2CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$

(b) 

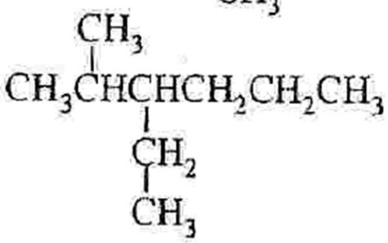
$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

(c) 

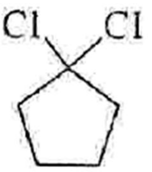
$CH_3CH_2CH_2\underset{\underset{\displaystyle CH_3}{\underset{|}{\displaystyle CHCH_3}}}{\underset{|}{C}}HCH_2CH_2CH_3$

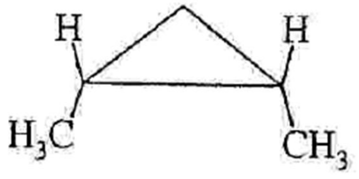
(d) 

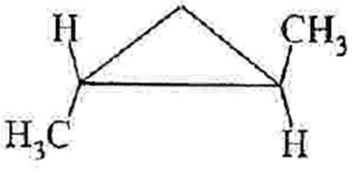
$CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$

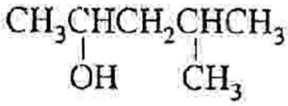
(e) 

$CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}H\underset{\underset{\displaystyle CH_3}{\underset{|}{\displaystyle CH_2}}}{\underset{|}{C}}HCH_2CH_2CH_3$

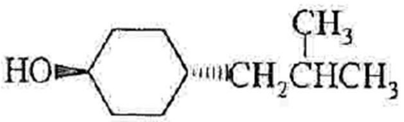
(f) 

(g) 

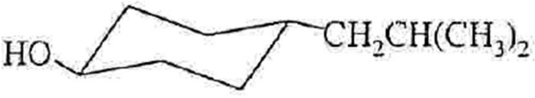
(h) 

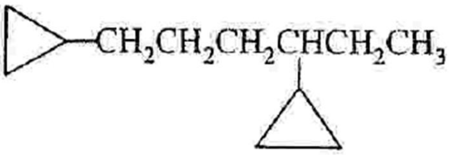
(i) 

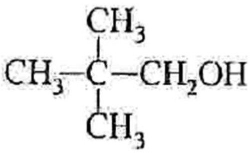
$\underset{OH}{CH_3CH}CH_2\underset{CH_3}{CH}CH_3$

(j) 

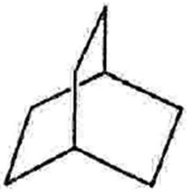
or

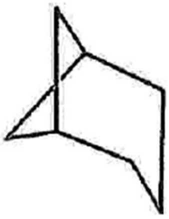


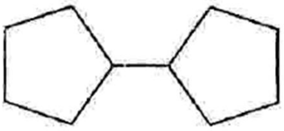
(k) 

(l) 

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH$

(m) 

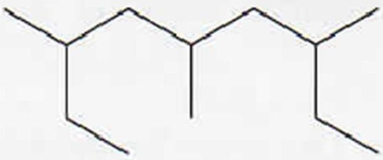
(n) 

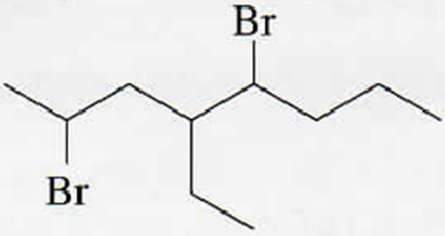
(o) 

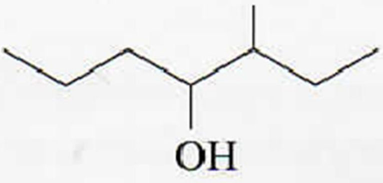
4.20 Aşağıdaki bileşiklerin IUPAC sistematik isimleri yazınız.

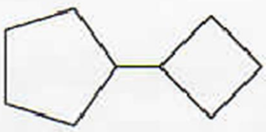
(a) $CH_3CH_2C(CH_3)_2CH(CH_2CH_3)CH_3$

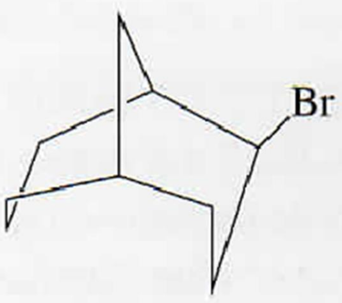
(b) $CH_3CH_2C(CH_3)_2CH_2OH$

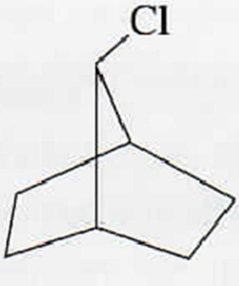
(c) 

(f) 

(d) 

(g) 

(e) 

(h) 

4.20 (a) 3,3,4-Trimethylhexane

(b) 2,2-Dimethyl-1-butanol

(c) 3,5,7-Trimethylnonane

(d) 3-Methyl-4-heptanol

(e) 2-Bromobicyclo[3.3.1]nonane

(f) 2,5-Dibromo-4-ethyloctane

(g) Cyclobutylcyclopentane

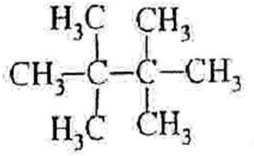
(h) 7-Chlorobicyclo[2.2.1]heptane

4.21 *sek*-Bütil alkol ismi özel bir yapıyı tanımlarken *sek*-pentil alkol adı belirli bir yapıyı göstermez. Niçin? Açıklayınız.

4.21 The two secondary carbon atoms in *sec*-butyl alcohol are equivalent; however, there are three five-carbon alcohols (pentyl alcohols) that contain a secondary carbon atom.

4.22 Aşağıdaki formüllere sahip alkan veya sikloalkanların yapılarını yazınız ve IUPAC sistematik isimlerini veriniz: **(a)** sadece birincil hidrojen atomları olan C_8H_{18}, **(b)** sadece ikincil hidrojen atomları içeren C_6H_{12}, **(c)** sadece birincil ve ikincil hidrojen atomları içeren C_6H_{12}, **(d)** 12 ikincil ve 2 üçüncül hidrojen içeren C_8H_{14}.

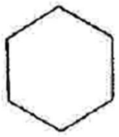
4.22 (a)



$$CH_3-\overset{H_3C}{\underset{H_3C}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

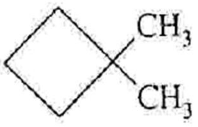
2,2,3,3 -Tetramethylbutane

(b)



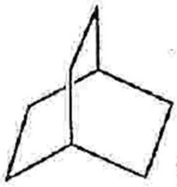
Cyclohexane

(c)



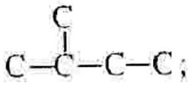
1,1-Dimethylcyclobutane

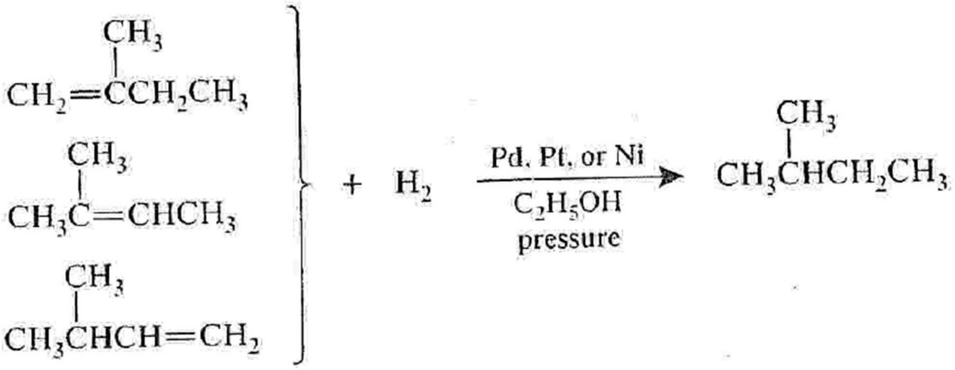
(d)



Bicyclo [2.2.2] octane

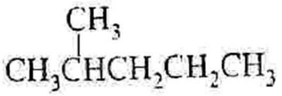
4.23 Üç farklı alken bir metal katalizör kullanılarak hidrojenlendirdiklerinde 2-metilbütan verirler. Bunların yapılarını ve tepkimelerini yazınız.

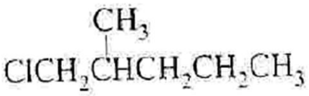
4.23 Each of the desired alkenes must have the same carbon skeleton as 2-methylbutane,  $C-\overset{C}{\overset{|}{C}}-C-C$; they are therefore

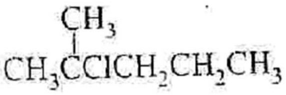


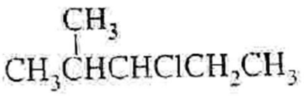
4.24 C_6H_{14} formülüne sahip bir alkan, altı farklı alkil halojenürün ($C_6H_{13}Cl$) çinko ve sulu asitlerle tepkimesiyle (aynı tepkimelerle) sentezlenebilir. Alkanın ve alkil halojenürlerin yapılarını yazınız.

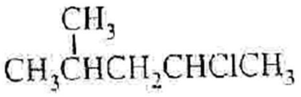
4.24 Only one isomer of C_6H_{14} can be produced from five isomeric hexyl chlorides ($C_6H_{13}Cl$).

The alkane is 2-methylpentane,  $CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$. The five alkyl chlorides are

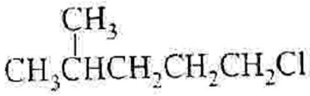

$ClCH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$


$CH_3\overset{CH_3}{\overset{|}{C}}ClCH_2CH_2CH_3$

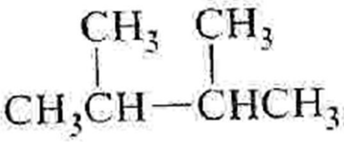

$CH_3\overset{CH_3}{\overset{|}{C}}HCHClCH_2CH_3$


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CHClCH_3$

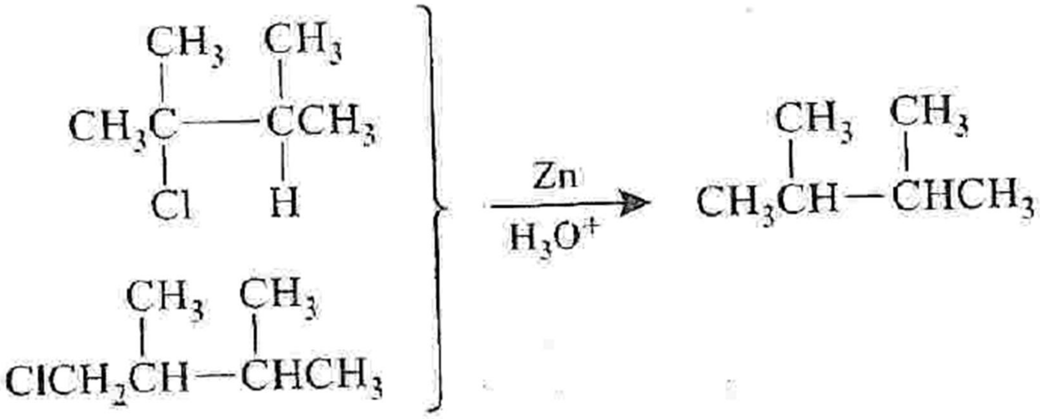
and


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_2Cl$

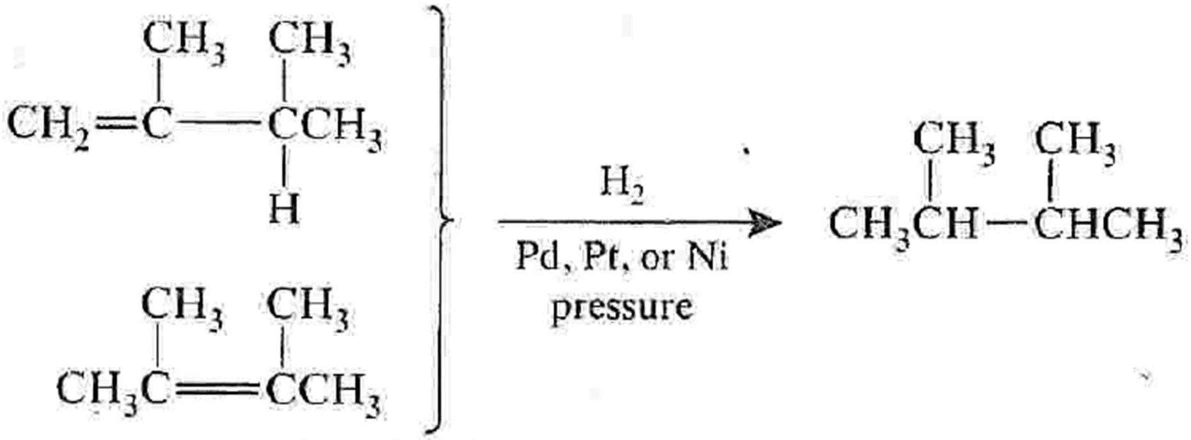
4.25 C_6H_{14} formülüne sahip bir alkan sadece iki alkil halojenürün ($C_6H_{13}Cl$) indirgenmesinden (Zn ve HCl ile) ve sadece iki alkenin (C_6H_{12}) hidrojenlenmesinden elde edilebilir. Bu alkanın yapısını, IUPAC ismini yazınız ve tepkimeleri gösteriniz.

4.25 
$CH_3\overset{CH_3}{\overset{|}{C}}H-\overset{CH_3}{\overset{|}{C}}HCH_3$ 2,3-Dimethylbutane

From two alkyl chlorides

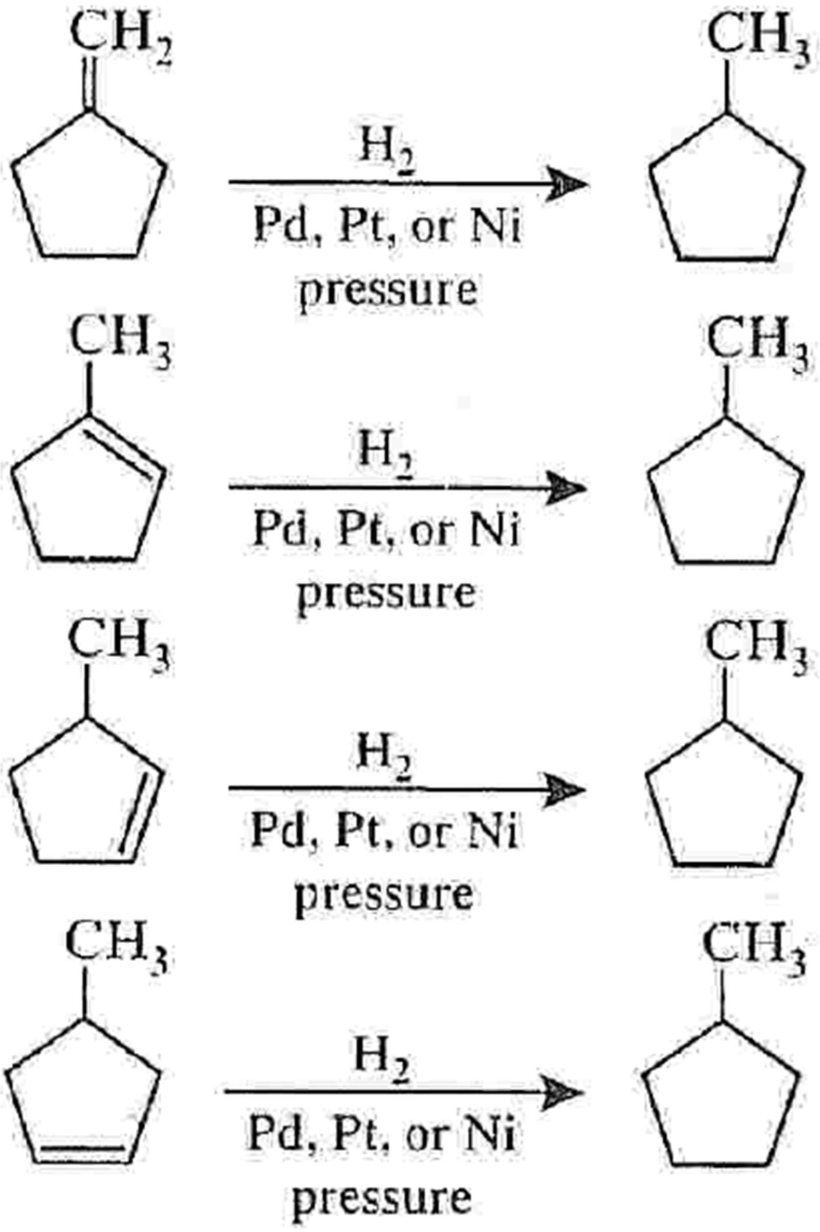


From two alkenes



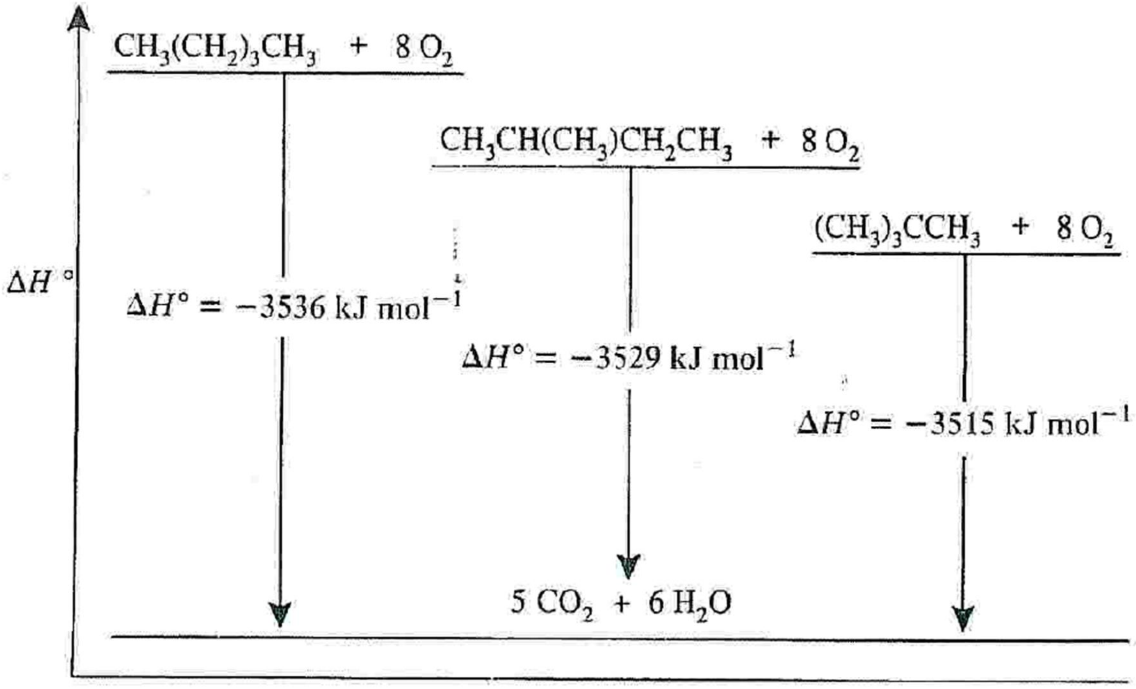
4.26 Dört farklı sikloalkenin her biri katalitik hidrojenleme sonucu metilsiklopentanı verecektir. Bunların yapılarını bulunuz. Tepkimeleri gösteriniz.

4.26



4.27 Üç pentan (C_5H_{12}) izomerinin yanma ısıları, $CH_3(CH_2)_3CH_3$ için 3536 kJ mol^{-1}, $CH_3CH(CH_3)CH_2CH_3$ için 3529 kJ mol^{-1}; ve $(CH_3)_3CCH_3$ için ise 3515 kJ mol^{-1} olarak verilmiştir. Hangi izomer en kararlıdır? Bu üç bileşiğin bağıl potansiyel enerjilerini gösteren, Şekil 4.9'daki gibi, bir diyagram çiziniz.

4.27 $(CH_3)_3CCH_3$ is the most stable isomer (i.e., it is the isomer with the lowest potential energy) because it evolves the least amount of heat on a molar basis when subjected to complete combustion.



$CH_3(CH_2)_3CH_3 + 8\ O_2$
$CH_3CH(CH_3)CH_2CH_3 + 8\ O_2$
$(CH_3)_3CCH_3 + 8\ O_2$
$\Delta H°$
$\Delta H° = -3536$ kJ mol^{-1}
$\Delta H° = -3529$ kJ mol^{-1}
$\Delta H° = -3515$ kJ mol^{-1}
$5\ CO_2 + 6\ H_2O$

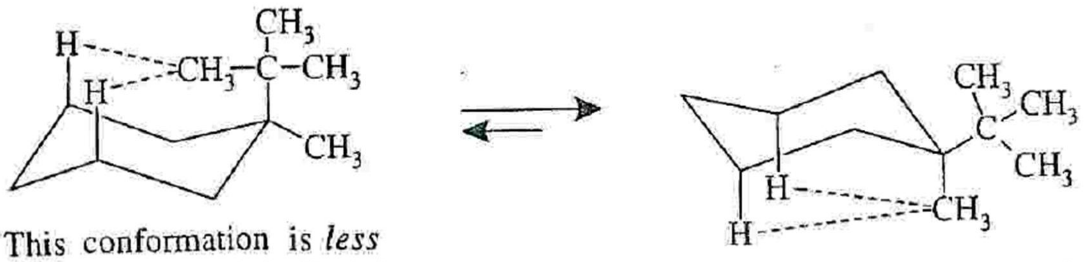
4.28 Homolog sıra nedir? Cevabınızı alkil halojenürlerin homolog serisini yazarak açıklayınız.

4.28 A homologous series is one in which each member of the series differs from the one preceding it by a constant amount, usually a CH_2 group. A homologous series of alkyl halides would be the following:

CH_3X
CH_3CH_2X
$CH_3(CH_2)_2X$
$CH_3(CH_2)_3X$
$CH_3(CH_2)_4X$
etc.

4.29 1-*ter*-Bütil-1-metilsikloheksanın iki sandalye konformasyonunun yapılarını çiziniz. Hangi konformasyon daha kararlıdır? Cevabınızı açıklayınız.

4.29

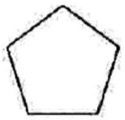


This conformation is *less stable* because 1,3-diaxial interactions with the large *tert*-butyl group cause considerable repulsion.

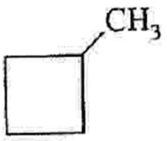
This conformation is *more stable* because 1,3-diaxial interactions with the smaller methyl group are less repulsive.

4.30 C_5H_{10} formülüne sahip tüm izomerlerin, ikili bağlı bileşikler hariç, yapı formüllerini ve isimlerini yazınız.

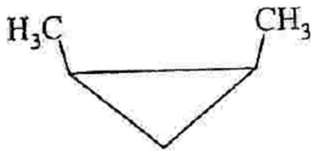
4.30



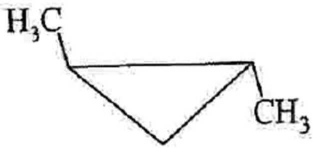
Cyclopentane



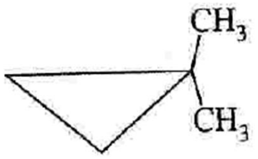
Methylcyclobutane



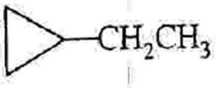
cis-1,2-Dimethylcyclopropane



trans-1,2-Dimethylcyclopropane



1,1-Dimethylcyclopropane



Ethylcyclopropane

4.31 Aşağıdaki bisiklik alkanların yapılarını yazınız.

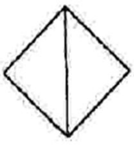
(a) Bisiklo[1.1.0]bütan

(b) Bisklo[2.1.0]pentan

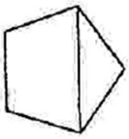
(c) 2-Klorobisiklo[3.2.0]heptan

(d) 7-Metilbisiklo[2.2.1]heptan

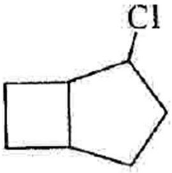
4.31 (a)



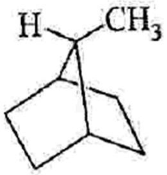
(b)



(c)



(d)

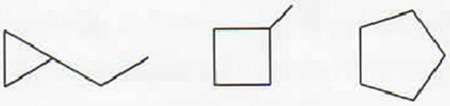


4.32 $S - A + 1 = N$ (Altbölüm 4.15) yöntemini kullanarak kubanın halka sayısını belirleyiniz.

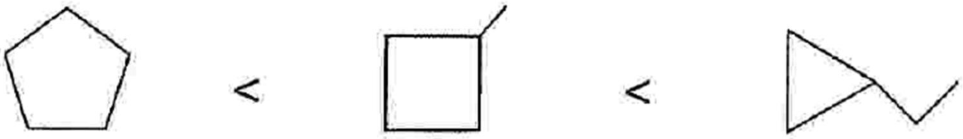
4.32 $S - A + 1 = N$

For cubane, $S = 12$ and $A = 8$. Thus $12 - 8 + 1 = N$; $N = 5$ rings in cubane.

4.33 Aşağıdaki bileşikleri **(a)** yanma ısılarının artışına, **(b)** artan kararlılıklarına göre sıralayınız.



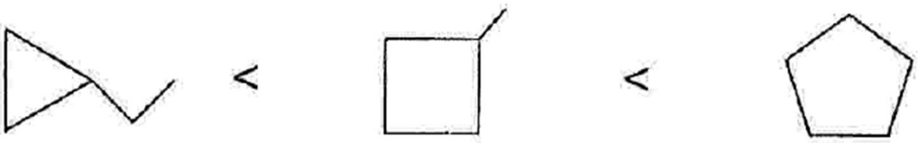
4.33 (a)



Smallest heat of combustion

Largest heat of combustion

(b)

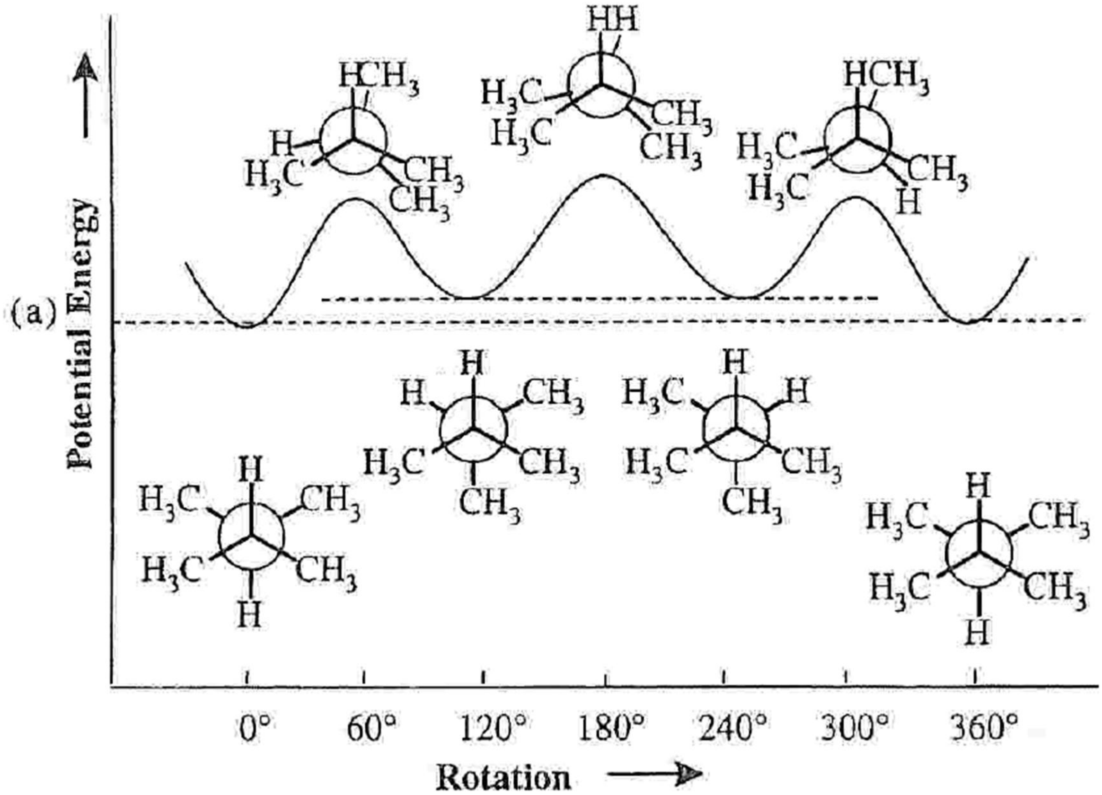


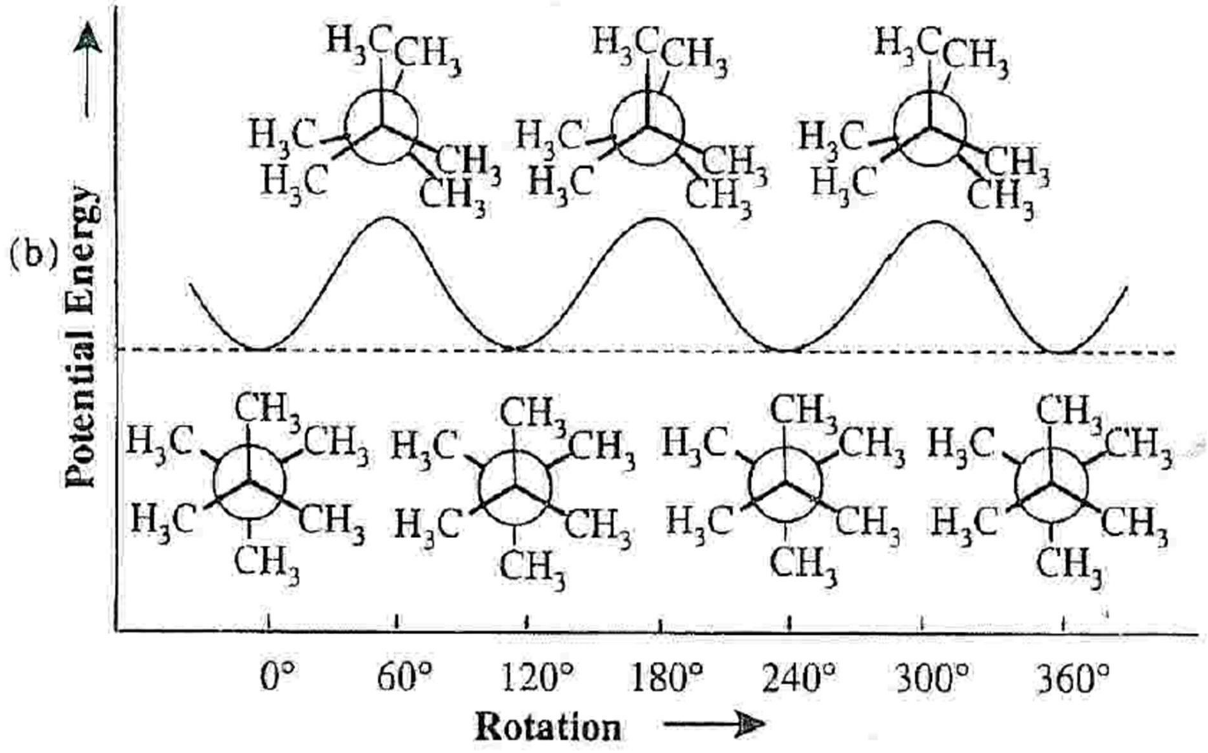
Least stable

Most stable

4.34 **(a)** 2,3-Dimetilbütan ve **(b)** 2,2,3,3-Tetrametilbütanın C2–C3 bağları etrafındaki dönmeden kaynaklanan enerji değişimlerini gösteren, Şekil 4.8'dekine benzer grafikler çiziniz. Enerji değişimlerinin sayısal değerleri ile ilgilenmenize gerek yoktur. Sadece tüm maksimum ve minimumlara uygun olan konformasyonları belirtmeniz gerekir.

4.34





4.35 Çizelgelerden yararlanmaksızın aşağıdaki çiftlerden hangisinin daha yüksek kaynama noktasına sahip olabileceğine karar veriniz. Cevabınızı açıklayınız.

(a) Pentan veya 2-metilbütan

(b) Heptan veya pentan

(c) Propan veya 2-kloropropan

(d) Bütan veya 1–propanol

(e) Bütan veya CH_3COCH_3

4.35 (a) Pentane would boil higher because its chain is unbranched. Chain-branching lowers the boiling point.

(b) Heptane would boil higher because it has the larger molecular weight and would, because of its larger surface area, have larger van der Waals attractions.

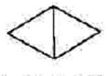
(c) 2-Chloropropane because it is more polar and because it has a larger molecular weight.

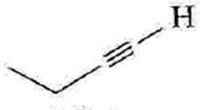
(d) 1-Propanol would boil higher because its molecules would be associated with each other through hydrogen-bond formation.

(e) Propanone (CH_3COCH_3) would boil higher because its molecules are more polar.

4.36 Molekül formülü C_4H_6 olan bileşik, bir bisiklik bileşiktir. Aynı formüle sahip bir başka bileşiğin IR spektrumunda 2250 cm^{-1} civarında bir soğurma piki vardır (bisiklik bileşiğin yok). Her iki bileşiğin yapılarını yazınız ve IR soğurmasının bu bileşikleri ayırt etmede nasıl kullanıldığını açıklayınız.

4.36 C_4H_6


Bicyclo[1.1.0]butane

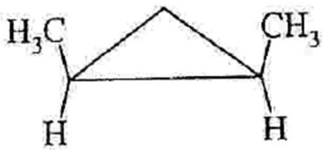


1-Butyne

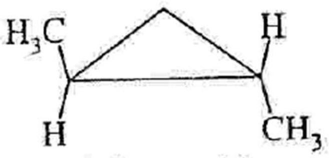
The IR stretch at ~2250 cm^{-1} for the alkyne C≡C bond distinguishes these two compounds.

4.37 Aşağıdaki bileşiklerden hangisinin daha kararlı olmasını beklersiniz? *cis*-1,2-dimetilsiklopropan veya *trans*-1,2-dimetilsiklopropan? Cevabınızı açıklayınız.

4.37 *trans*-1,2-Dimethylcyclopropane would be more stable because there is less crowding between its methyl groups.



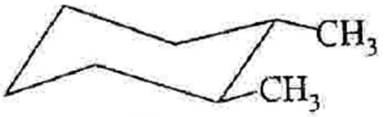
Less stable



More stable

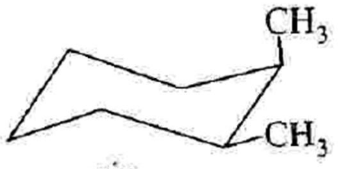
4.38 Aşağıdaki bileşik çiftlerinden hangisi daha yüksek yanma ısısına sahip olmalıdır? **(a)** *cis* veya *trans* –1,2-dimetilsikloheksan, **(b)** *cis* veya *trans* –1,3-dimetilsikloheksan, **(c)** *cis* veya *trans* –1,4-dimetilsikloheksan. Cevaplarınızı açıklayınız.

4.38 (a)



trans

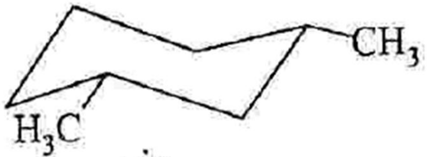
More stable because both methyl groups are equatorial in the most stable conformation



cis

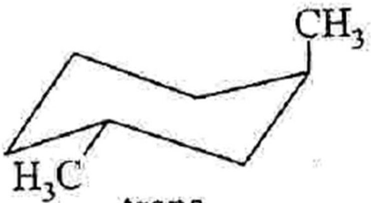
Less stable because one methyl group must be axial and so has the larger heat of combustion

(b)



cis

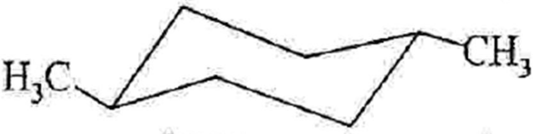
More stable because both methyl groups are equatorial in the most stable conformation



trans

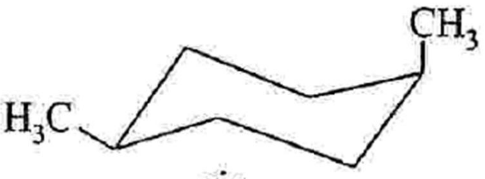
Less stable because one methyl group must be axial and so has the larger heat of combustion

(c)



trans

More stable because both methyl groups are equatorial in the most stable conformation

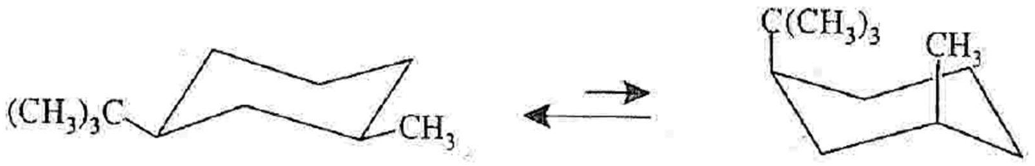


cis

Less stable because one methyl group must be axial and so has the larger heat of combustion

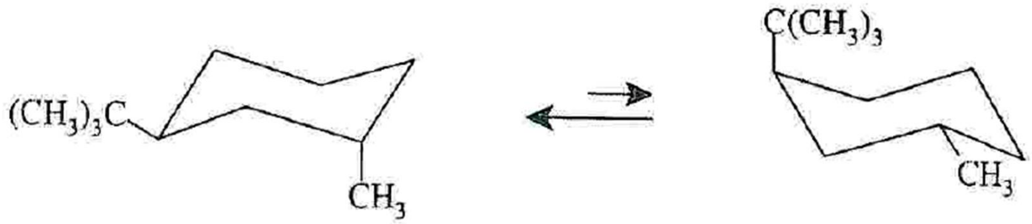
4.39 Aşağıdakilerin her birinin iki sandalye konformasyonunu çiziniz ve her biri için hangi konformasyonun daha kararlı olabileceğini belirtiniz. **(a)** *cis*-1-*ter*-bütil-3-metilsikloheksan **(b)** *trans*-1-*ter*-bütil-3-metilsikloheksan, **(c)** *trans*-1-*ter*-bütil-4-metilsikloheksan, **(d)** cis-1-*ter*-bütil-4-metilsikloheksan

4.39 (a)



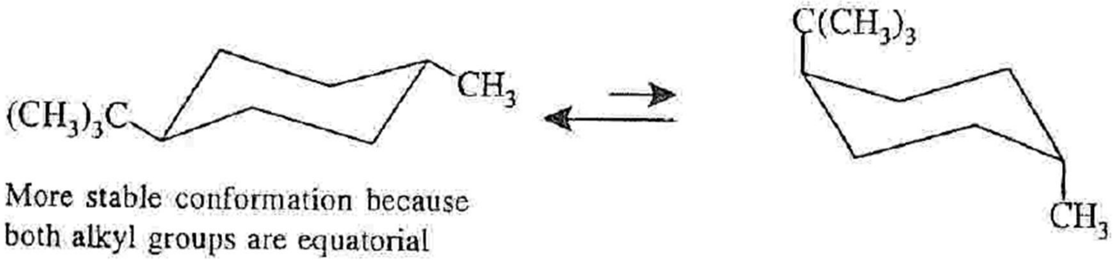
More stable conformation because both alkyl groups are equatorial

(b)



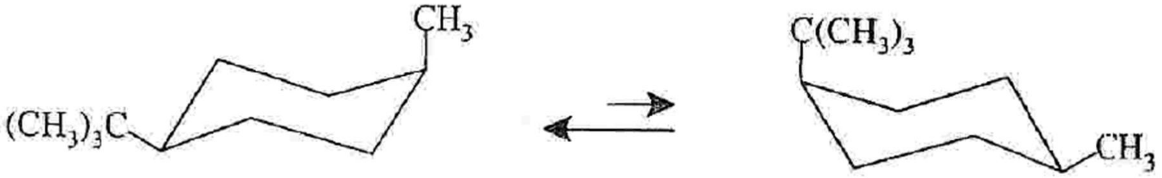
More stable because larger group is equatorial

(c)



More stable conformation because both alkyl groups are equatorial

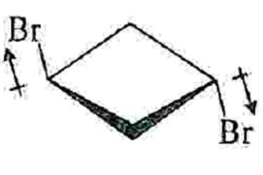
(d)



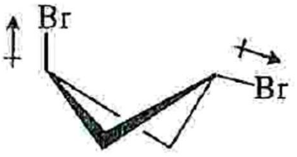
More stable because larger group is equatorial

4.40 *trans*-1,3-Dibromosiklobütanın ölçülebilir bir dipol momenti vardır. Bu sonuç siklobütan halkasının düzlem yapıda olmadığını gösterir. Niçin? Açıklayınız.

4.40 If the cyclobutane ring were planar, the C−Br bond moments would exactly cancel in the trans isomer. The fact that *trans*-1,3-dibromocyclobutane has a dipole moment shows the ring is not planar.



Planar form
$\mu = 0$

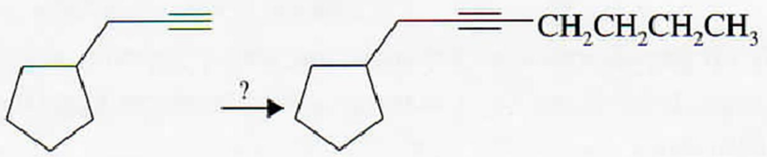


Bent form
$\mu \neq 0$

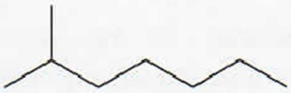
4.41 Aşağıdaki sentezlerde eksik olan bileşik ve/veya reaktantları yazınız (bazı durumlarda birden fazla basamak gerekli olabilir):

(a) *trans*-5-Metil-2-heksen $\xrightarrow{?}$ 2-metilheksan

(b)

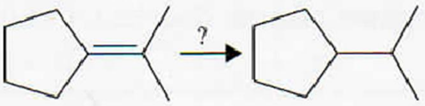


(c) $CH_3CH_2CH_2Br \xrightarrow{?}$



(d) 4-Bromo-3,4-dietilheptan $\xrightarrow{Zn,\ HBr}$?

(e)

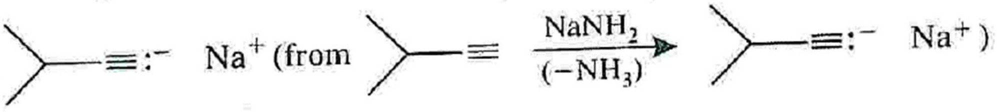


(f) ? $\xrightarrow{Zn,\ HX}$ 2,2-dimetilpropan

4.41 (a) H_2; Pd, Pt, or Ni catalyst, pressure

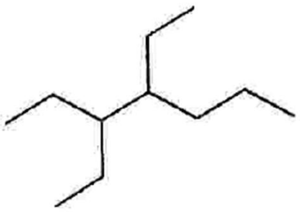
(b) (1) $NaNH_2$ (2) $BrCH_2CH_2CH_2CH_3$

(c) (1)



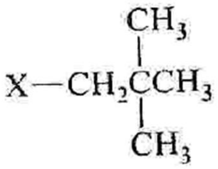
(2) H_2; Pd, Pt, or Ni catalyst, pressure

(d)



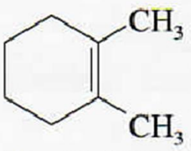
(e) H_2; Pd, Pt, or Ni catalyst, pressure

(f)



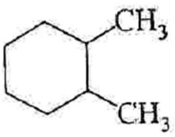
$$X-CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_3$$

***4.42** 1,2-Dimetilsikloheksan (aşağıda) platin katalizör varlığında hidrojen ile tepkime verdiğinde –50°C'da eriyen ve 130°C'da (760 torr) kaynayan bir sikloalkan meydana gelir. **(a)** Bu tepkime ürününün yapısını bulunuz. **(b)** Uygun çizelgeden karşılaştırarak hangi izomer olduğunu belirtiniz. **(c)** Bu deney size, hidrojenin ikili bağa katılma şekli hakkında hangi bilgiyi verir.



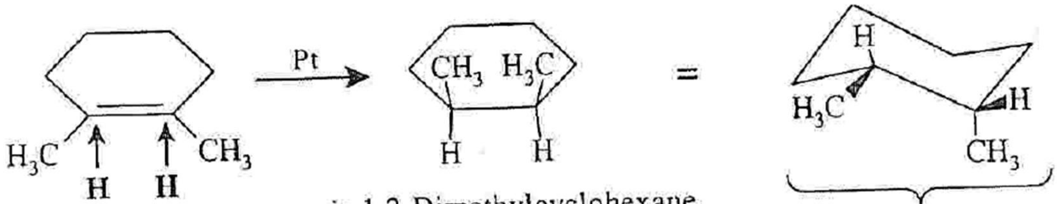
1,2-Dimetilsikloheksen

*4.42 (a)



(b) From Table 4.8 we find that this is *cis*-1,2-dimethylcyclohexane.

(c) Since catalytic hydrogenation produces the cis isomer, both hydrogen atoms must have added from the same side of the double bond. (As we shall see in Section 7.14, this type of addition is called a syn addition.



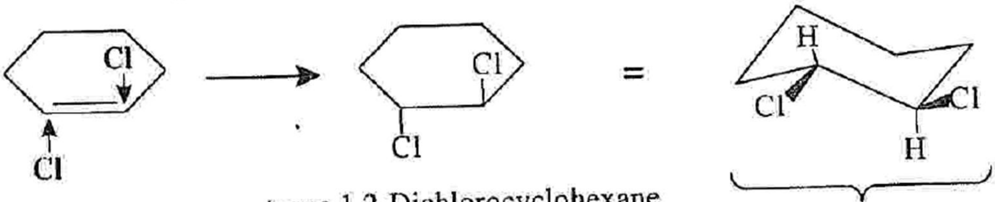
cis-1,2-Dimethylcyclohexane

The cis isomer is produced when both hydrogen atoms add from the same side.

***4.43** Uygun bir çözücü içerisinde sikloheksanın klor ile tepkimesinden formülü $C_6H_{10}C_2$, erime noktası –7°C, kaynama noktası (16 torr) 74°C olan bir ürün meydana gelir. (a) Bu hangi stereoizomerdir? (b) Bu deney klorun ikili bağa katılma şekli konusunda hangi bilgiyi verir?

***4.43** (a) From Table 4.8 we find that this is *trans*-1,2-dichlorocyclohexane.

(b) Since the product is the trans isomer, we can conclude that the chlorine atoms have added from opposite sides of the double bond.



trans-1,2-Dichlorocyclohexane

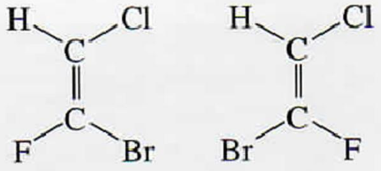
The trans isomer is produced when the chlorine atoms add from opposite sides of the double bond.

4.44 1,3-Di-*ter*-bütilsikloheksanın cis ve trans izomerlerini ele alalım (molekül modelleri oluşturunuz). Hangi alışılmamış durum, izomerlerden bir tanesinin sandalye konformasyonu yerine burkulmuş kayık konformasyonunda bulunmasının nedenidir?

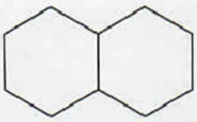
4.44 If *trans*-1,3-di-*tert*-butylcyclohexane were to adopt a chair conformation, one *tert*-butyl group would have to be axial. It is, therefore, more energetically favorable for the molecule to adopt a twist boat conformation.

***4.45** Bu bölümde öğrendiğiniz kurallara göre aşağıdakilerin sistematik adlarını yazınız veya daha fazla kurala gerek olan yapıları belirtiniz.

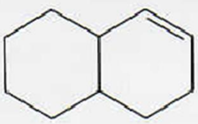
(a)



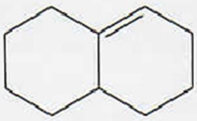
(b)



(c)



(d)

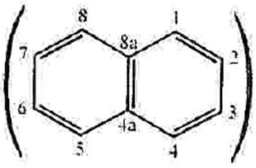


*4.45 (a) More rules are needed (see Chapter 7) to indicate relative stereochemistry for these 1-bromo-2-chloro-1-fluoroethenes.

(b) Bicyclo[4.4.0]decane (or decalin)

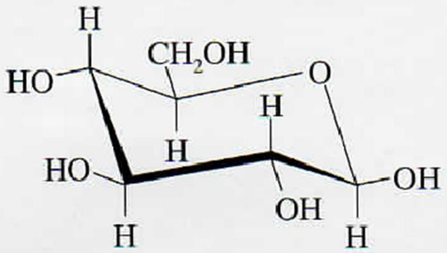
(c) Bicyclo[4.4.0]dec-2-ene (or Δ^1-octalin)

(d) Bicyclo[4.4.0]dec-1-ene (or $\Delta^{1(8a)}$-octalin)

NOTE: The common name decalin comes from decahydronaphthalene, the derivative of naphthalene () that has had all of its five double bonds converted to single bonds by addition of 10 atoms of hydrogen. Octalin similarly comes from octahydronaphthalene and contains one surviving double bond. When using these common names derived from naphthalene, their skeletons are usually numbered like that of naphthalene. When, as in case (d), a double bond does not lie between the indicated carbon and the next higher numbered carbon, its location is specified as shown.

Also, the symbol Δ is one that has been used with commom names to indicate the presence of a double bond at the position specified by the accompanying superscript number(s).

***4.46** Aşağıdaki yapı *D*-glikozun baskın konformasyonudur.



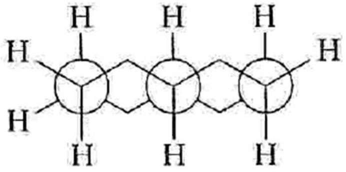
D-glikoz doğada en yaygın bulunan şekerdir. Bu sonuç şaşırtıcı değildir. Niçin? Açıklayınız. (ipucu: *D*-galaktoz ve *D*-mannoz gibi şekerlerin yapılarını *D*-glikozunki ile karşılaştırınız.)

*4.46 D-Glucose has all of its attached groups equatorial in the lowest energy chair conformation. Other sugars have at least one group axial in their lowest energy chair conformation.

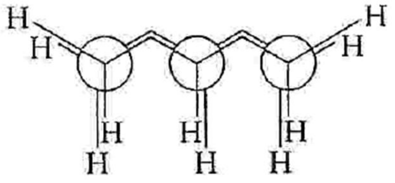
Because if the configuration of stereocenters is changed, not all of the ring substituents can simultaneously be in the preferred equatorial position, as they are in glucose.

***4.47** Newman izdüşümlerini kullanarak *cis-* ve *trans-* dekalinin köprü başı atomlarındaki sübstitüentlerin bağıl konumlarını çiziniz. Bu izomerlerden hangisinin daha kararlı olmasını beklersiniz, niçin?

*4.47



trans



cis

The *trans* isomer would be more stable because it can have both of its rings in the favored chair conformation, avoiding the many eclipsing interactions found in the doubly boat conformation of the *cis* isomer (which would actually increase its stability slightly by twisting to avoid some eclipsing interactions).

***4.48** En fazla dört karbonlu herhangi iki bileşikten çıkarak dodekan, $CH_3(CH_2)_{10}CH_3$, sentezi için eşitlikleri yazınız.

*4.48 $H{-}C{\equiv}C{-}C{\equiv}C{-}H \xrightarrow[\text{2 mol equiv. } CH_3(CH_2)_3Br]{\text{2 mol equiv. } LiNH_2}$

$$CH_3(CH_2)_3{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_3CH_3 \xrightarrow[\text{Pt catalyst}]{H_2} CH_3(CH_2)_{10}CH_3$$

Stereokimya: Kiral Moleküller

Aşağıdaki nesnelerin her birini kiral veya akiral oluşlarına göre sınıflandırınız. **Problem 5.1**

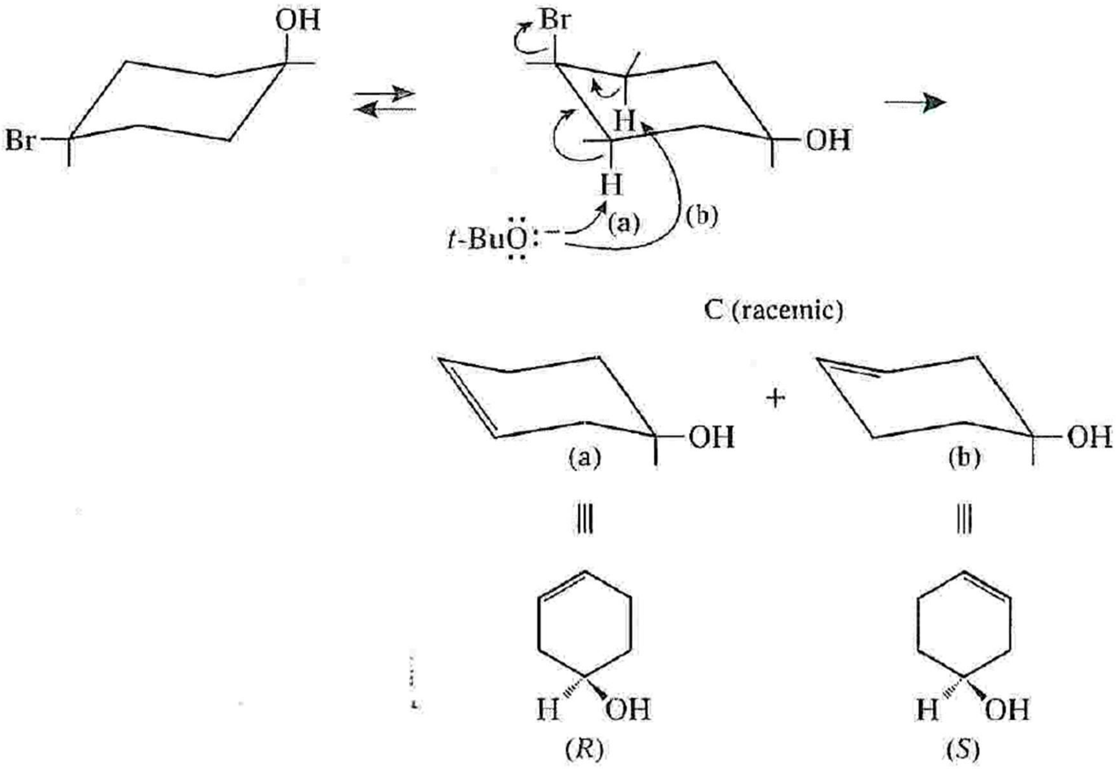
(a) Tornavida
(b) Beyzbol sopası
(c) Golf sopası
(d) Tenis ayakkabısı
(e) Kulak
(f) Odun vidası
(g) Otomobil
(h) Çekiç

5.1 (a) Achiral (c) Chiral (e) Chiral (g) Chiral
(b) Achiral (d) Chiral (f) Chiral (h) Achiral

Eğer modelleriniz varsa, Şekil 5.3'te gösterilen 2-bütanol modellerini kurunuz ve gerçekten çakışmaz olduklarını kendiniz görünüz. (a) Benzer modelleri 2-bromopropan için kurunuz. Onlar çakışıyorlar mı? (b) 2-Bromopropan molekülü kiral midir? (c) 2-Bromopropanın enantiyomerik yapılarını bulmayı umuyor musunuz? **Problem 5.2**

5.2 (a) Yes (b) No (c) No

***6.46** The IR evidence indicates that C possesses both an alkene function and a hydroxyl group. An E2 reaction on this substrate produces enantiomeric unsaturated alcohols.

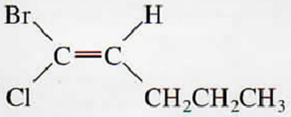


Alkenler ve Alkinler I: Özellikleri ve Elde Edilişleri. Alkil Halojenürlerin Ayrılma Tepkimeleri

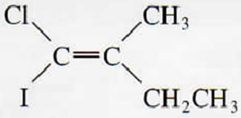
Problem 7.1

(*E*)–(*Z*) Adlandırma sistemini kullanarak [ayrıca, (e) ve (f) şıklarında (*R*–*S*) adlandırma sistemini de gözönüne alarak) aşağıdaki her bir bileşiğin IUPAC adını yazınız.

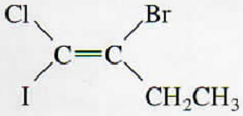
(a)



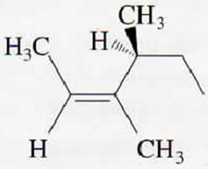
(d)



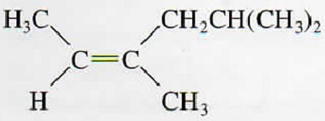
(b)



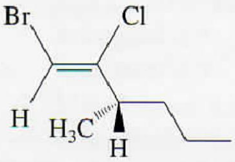
(e)



(c)



(f)



7.1 (a) (*E*)-1-Bromo-1-chloro-1-pentene

(b) (*E*)-2-Bromo-1-chloro-1-iodo-1-butene

(c) (*Z*)-3,5-Dimethyl-2-hexene

(d) (*Z*)-1-Chloro-1-iodo-2-methyl-1-butene

(e) (*Z*,4*S*)-3,4-Dimethyl-2-hexene

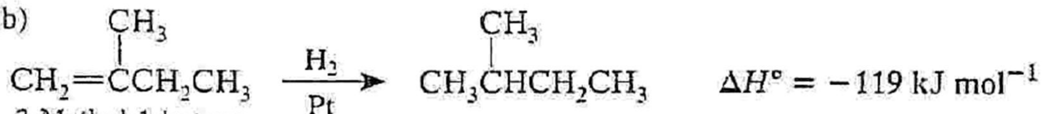
(f) (*Z*,3*S*)-1-Bromo-2-chloro-3-methyl-1-hexene

Problem 7.2 ➤ Üç alkenin hidrojenlenme ısıları aşağıdaki gibidir:

2-metil-1-büten	(– 119 kJ mol^{-1})
3-metil-1-büten	(– 127 kJ mol^{-1})
2-metil-2-büten	(– 113 kJ mol^{-1})

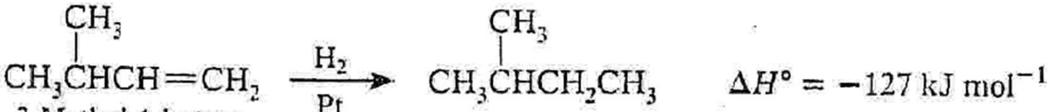
(a) Her bir alkenin molekül yapısını yazınız ve molekülün ikili bağlı karbon atomlarını, monosübstitüe, disübstitüe, trisübstitüe veya tetrasübstitüe oluşuna göre sınıflandırınız. (b) Her bir alken hidrojenlendiğinde oluşan ürünün molekül yapısını çiziniz. (c) Hidrojenlenme ısıları, bu üç alkenin bağıl kararlılıkları arasında bir bağlantı kurmak için kullanılabilir mi? (d) Eğer öyleyse, tahmin edilen kararlılık sırası nedir? Eğer değilse, Neden? (e) Bu alkenler için hangi diğer alken izomerleri mümkündür? Bu izomerlerin molekül yapılarını yazınız. (f) Bütün bu alkenlerin kararlılıkları arasında bir bağlantı kurmak için hangi veriler gereklidir?

7.2 (a), (b)



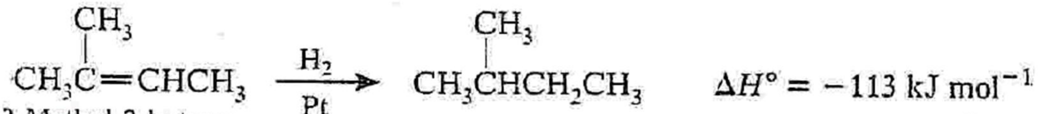
$$CH_2{=}\overset{CH_3}{\overset{|}{C}}CH_2CH_3 \xrightarrow[Pt]{H_2} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_3 \qquad \Delta H^\circ = -119\ kJ\ mol^{-1}$$

2-Methyl-1-butene
(disubstituted)



$$CH_3\overset{CH_3}{\overset{|}{C}}HCH{=}CH_2 \xrightarrow[Pt]{H_2} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_3 \qquad \Delta H^\circ = -127\ kJ\ mol^{-1}$$

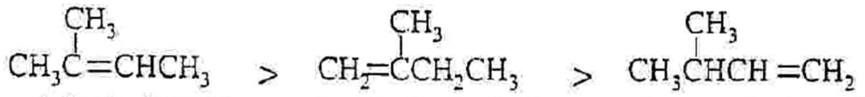
3-Methyl-1-butene
(monosubstituted)



$$CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_3 \xrightarrow[Pt]{H_2} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_3 \qquad \Delta H^\circ = -113\ kJ\ mol^{-1}$$

2-Methyl-2-butene
(trisubstituted)

(c) Yes, because hydrogenation converts each alkene into the same product.

(d) 

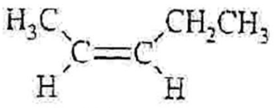
$$CH_3C(CH_3)=CHCH_3 > CH_2=C(CH_3)CH_2CH_3 > CH_3CH(CH_3)CH=CH_2$$

(trisubstituted) (disubstituted) (monosubstituted)

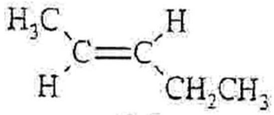
Notice that this predicted order of stability is confirmed by the heats of hydrogenation. 2-Methyl-2-butene evolves the least heat; therefore, it is the most stable. 3-Methyl-1-butene evolves the most heat; therefore, it is the least stable.

(e) $CH_2=CHCH_2CH_2CH_3$

1-Pentene



cis-2-Pentene



trans-2-Pentene

(f) Heats of combustion, because complete combustion would convert all of the alkenes to the same products. (All of the alkenes have the formula C_5H_{10}.)

$$C_5H_{10} + 7\,1/2\ O_2 \longrightarrow 5\ CO_2 + 5\ H_2O$$

Problem 7.3

Aşağıda verilen her bir alken çiftinden daha kararlı olanını tahmin ediniz. (a) 2-Metil-2-penten veya 2,3-dimentil-2-büten, (b) *cis*-3-heksen veya *trans*-3-heksen, (c) 1-heksen veya *cis*-3-heksen ve (d) *trans*-2-heksen veya 2-metil-2-penten.

7.3 (a) 2,3-Dimethyl-2-butene would be the more stable because the double bond is tetrasubstituted. 2-Methyl-2-pentene has a trisubstituted double bond.

(b) *trans*-3-Hexene would be the more stable because alkenes with trans double bonds are more stable than those with cis double bonds.

(c) *cis*-3-Hexene would be more stable because its double bond is disubstituted. The double bond of 1-hexene is monosubstituted.

(d) 2-Methyl-2-pentene would be the more stable because its double bond is trisubstituted. The double bond of *trans*-2-hexene is disubstituted.

Problem 7.4

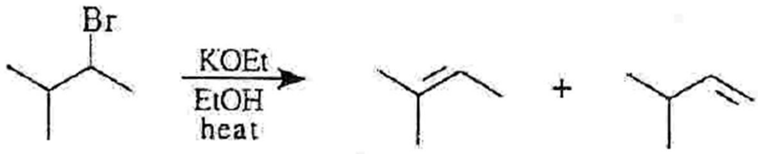
Problem 7.3'te verilen alken çiftlerini tekrar ele alınız. Hidrojenlenme ısılarını kullanarak bağıl kararlılıkları belirlemek için hangi alken çiftlerini kullanabilirsiniz? Yanma ısılarını kullanmak için hangi çiftlere gerek duyarsınız?

7.4 The relative stabilities of the pairs of alkenes in parts (b) and (c) in Problem 7.3 could be determined by measuring heats of hydrogenation, because in each instance the two alkenes would yield the same product. Heats of combustion could be used to determine the relative stabilities of the alkene pairs in parts (a) and (d) [and also those in parts (b) and (c)] because on complete combustion the alkenes produce the same number of molar equivalents of CO_2 and H_2O.

Problem 7.5

Aşağıdaki alkil halojenürlerin her birinden, etanol içerisinde potasyum hidroksitle hidrojen halojenür çıkarılmasıyla oluşturulan alkenleri sıralayınız ve Zaitsev kuralını kullanarak her bir tepkimenin ana ürününü tahmin ediniz. (a) 2-bromo-3-metilbütan ve (b) 2-bromo-2,3-dimetilbütan.

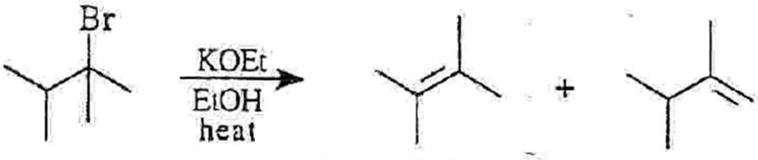
7.5 (a)



(trisubstituted, more stable)
Major product

(monosubstituted, less stable)
Minor product

(b)



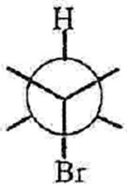
(tetrasubstituted, more stable)
Major product

(disubstituted, less stable)
Minor product

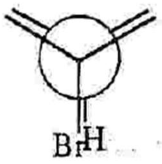
Problem 7.6

Etil bromür gibi bir molekülü ele alınız ve, anti periplanar geçiş halinin sin periplanar şekline göre daha çok yeğleneceğini Newman izdüşümü ile gösteriniz.

7.6 An anti periplanar transition state allows the molecule to assume the more stable staggered conformation,



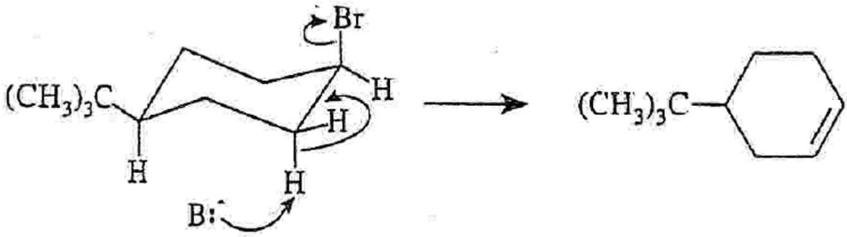
whereas a syn periplanar transition state requires the molecule to assume the less stable eclipsed conformation:



Problem 7.7

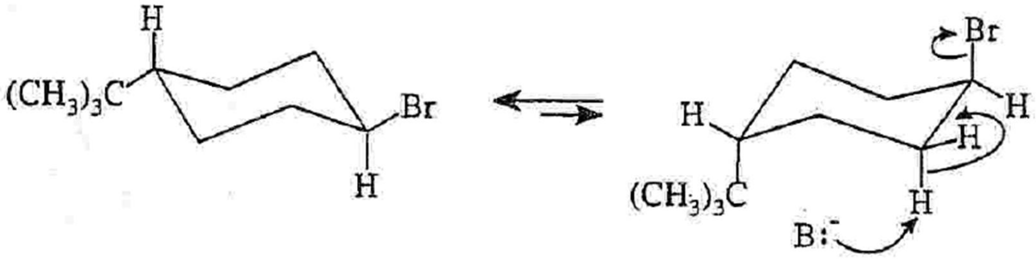
cis-1-Bromo-4-*ter*-bütilsikloheksan etanol içerisinde sodyum etoksitle etkileştirildiğinde hızla tepkime verir ve ürün 4-*ter*-bütilsikloheksendir. Aynı koşullar altında, *trans*-1-bromo-4-*ter*-bütilsikloheksan çok yavaş tepkime verir. Konformasyon yapılarını yazarak, bu *cis*- ve *trans*- izomerlerin etkinliklerindeki değişikliği açıklayınız.

7.7 *cis*-1-Bromo-4-*tert*-butylcyclohexane can assume an anti periplanar transition state in which the bulky *tert*-butyl group is equatorial:



The conformation (above), because it is relatively stable, is assumed by most of the molecules present, and, therefore, the reaction is rapid.

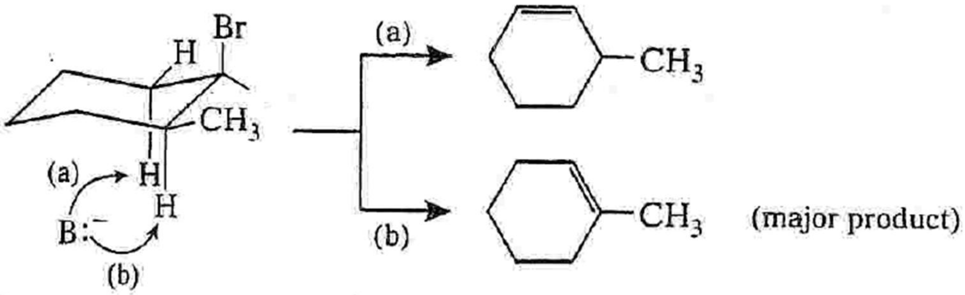
On the other hand, for *trans*-1-bromo-4-*tert*-butylcyclohexane to assume an anti periplanar transition state, the molecule must assume a conformation in which the large *tert*-butyl group is axial:



Such a conformation is of high energy; therefore, very few molecules assume this conformation. The reaction, consequently, is very slow.

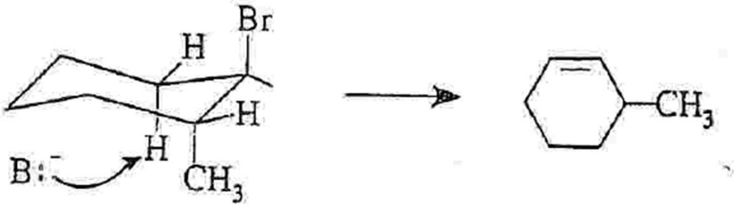
(a) *cis*-1-Bromo-2-metilsikloheksan bir E2 tepkimesi verdiğinde iki ürün (sikloalkenler) oluşur. Bu sikloalkenlar hangileridir ve ana ürünün hangisi olmasını beklersiniz? Her birinin nasıl oluştuğunu göstermek için konformasyon yapılarını yazınız. (b) *trans*-1-Bromo-2-metilsikloheksan bir E2 tepkimesi verdiğinde, yalnız bir sikloalkan oluşur. Bu ürün nedir? Konformasyon yapılarını yazarak, niçin bu ürünün tek ürün olarak oluştuğunu gösteriniz. ◄ **Problem 7.8**

7.8 (a) Anti periplanar elimination can occur in two ways with the cis isomer.



cis-1-Bromo-2-methylcyclohexane

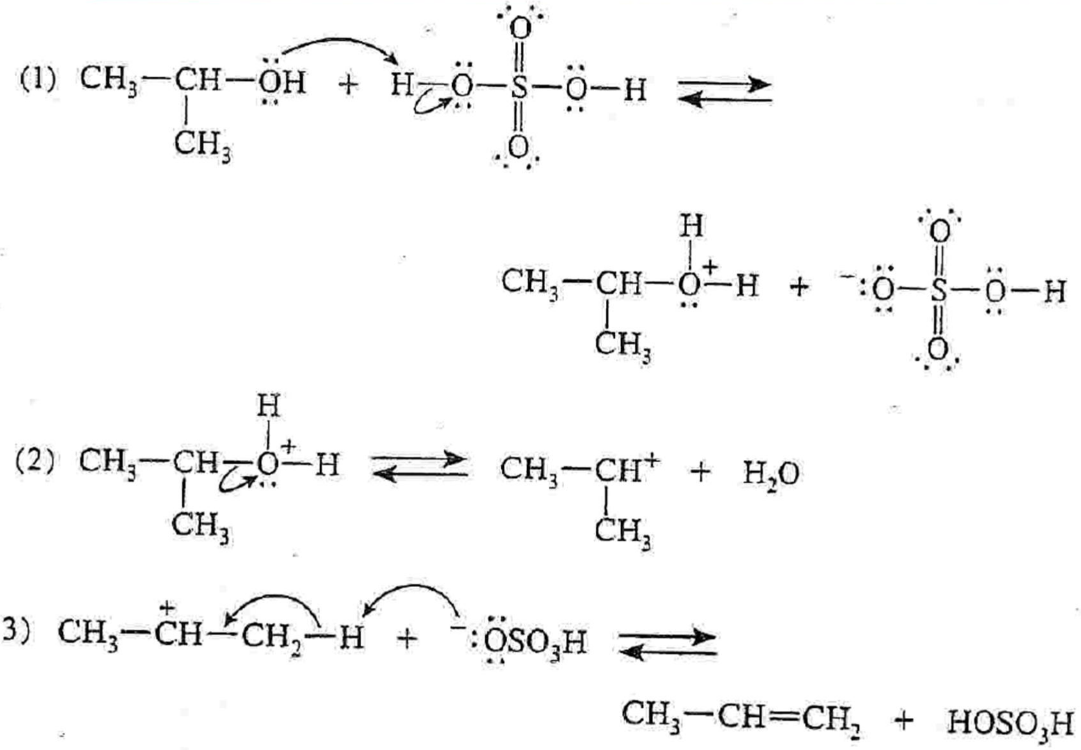
(b) Anti periplanar elimination can occur in only one way with the trans isomer.



trans-1-Bromo-2-methylcyclohexane

Problem 7.9 ➤ 2-Propanolden su çıkarılması, %75 lik H_2SO_4 içerisinde 100°C'da meydana gelir. (a) Eğri okları kullanarak su çıkarılması tepkimesinin mekanizmasını tüm basamaklarıyla yazınız. (b) Alkollerden su çıkarılması tepkimesinde asit katalizörün rolünü açıklayınız. (*İpucu:* Eğer ortamda asit bulunmasaydı ne olacağını düşününüz.)

7.9 (a)



$$(1)\quad CH_3-\underset{CH_3}{CH}-\ddot{O}H + H-\ddot{O}-\overset{O}{\underset{O}{S}}-\ddot{O}-H \rightleftharpoons CH_3-\underset{CH_3}{CH}-\overset{H}{\overset{+}{O}}-H + {}^-:\ddot{O}-\overset{O}{\underset{O}{S}}-\ddot{O}-H$$

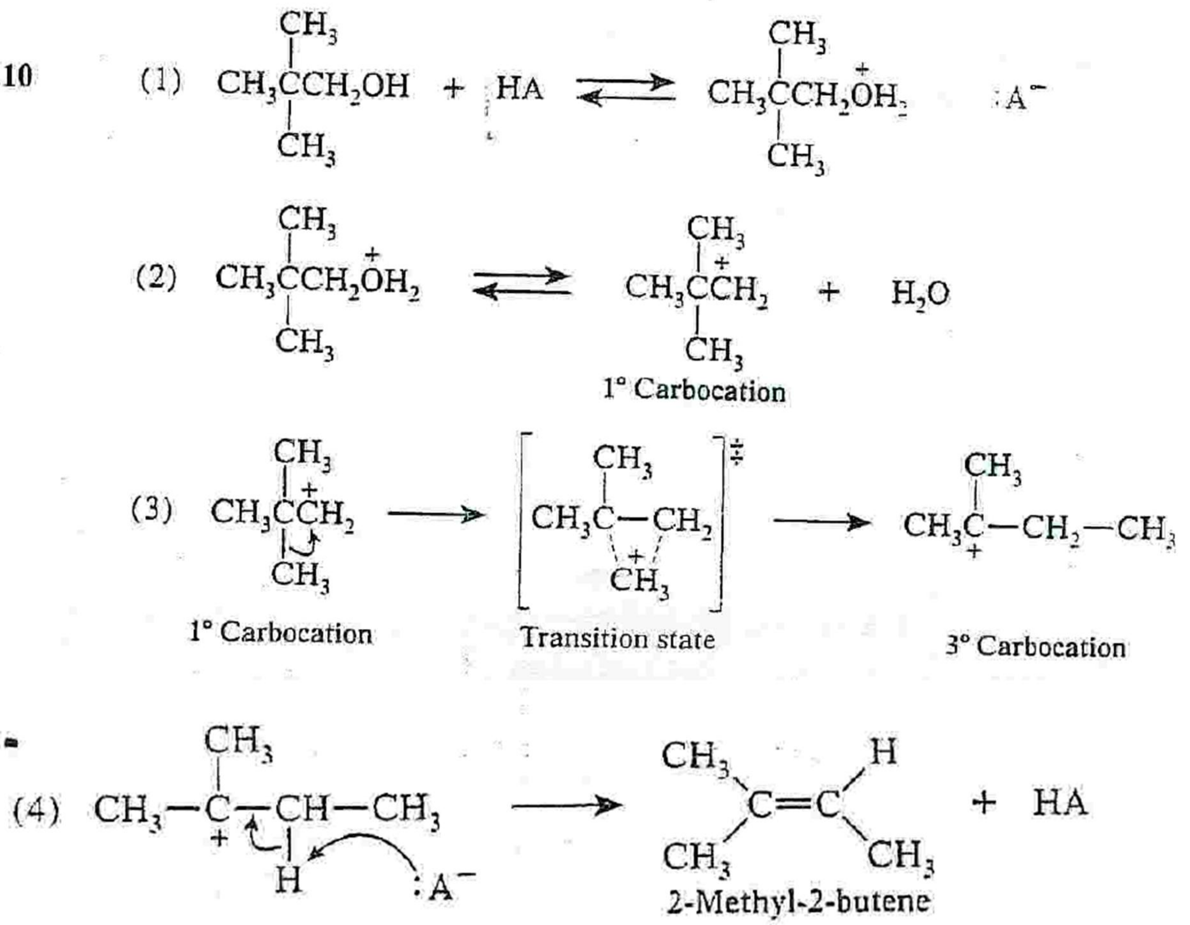
$$(2)\quad CH_3-\underset{CH_3}{CH}-\overset{H}{\overset{+}{O}}-H \rightleftharpoons CH_3-\underset{CH_3}{CH^+} + H_2O$$

$$(3)\quad CH_3-\overset{+}{C}H-CH_2-H + {}^-:\ddot{O}SO_3H \rightleftharpoons CH_3-CH=CH_2 + HOSO_3H$$

(b) By donating a proton to the $-OH$ group of the alcohol in step (1), the acid allows the loss of a relatively stable, weakly basic, leaving group (H_2O) in step (2). In the absence of an acid, the leaving group would have to be the strongly basic OH^- ion, and such steps almost never occur.

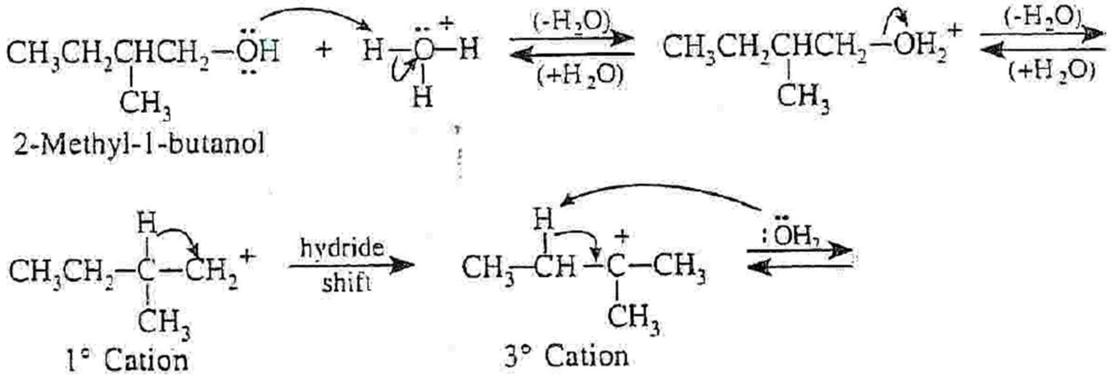
Neopentil alkolün, $(CH_3)_3CCH_2OH$, asit katalizli su çıkarılması tepkimesi ana ürün olarak 2-metil-2-büten oluşturmaktadır. Bu ürünün oluşumundaki bütün basamakları gösteren bir mekanizma tasarlayınız. ◄ **Problem 7.10**

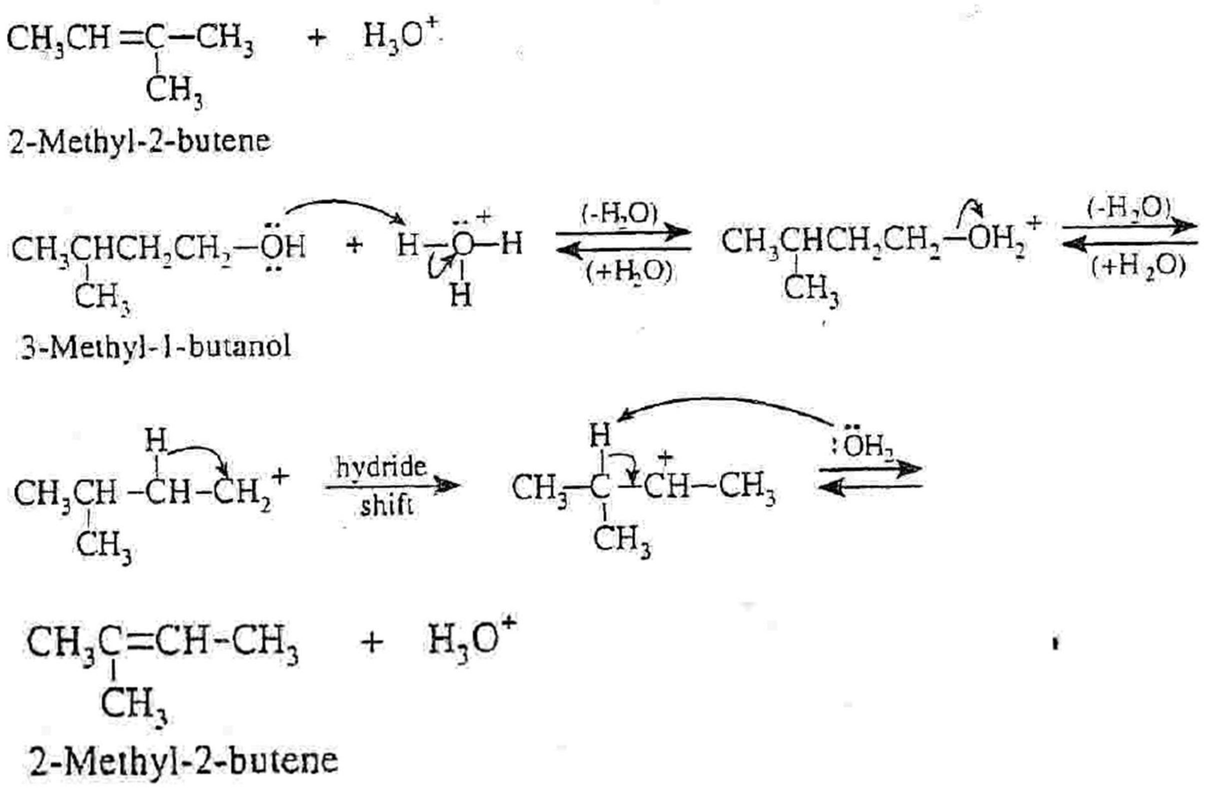
7.10



2-Metil-1-bütanol veya 3-metil-1-bütanolün asit katalizli su çıkarılması tepkimesi ana ürün olarak 2-metil-2-büten oluşturmaktadır. Bu sonuçları açıklayan uygun mekanizmaları yazınız. **Problem 7.11**

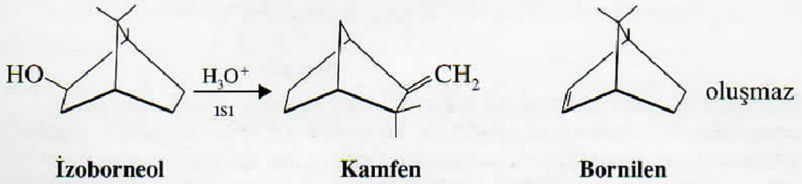
7.11



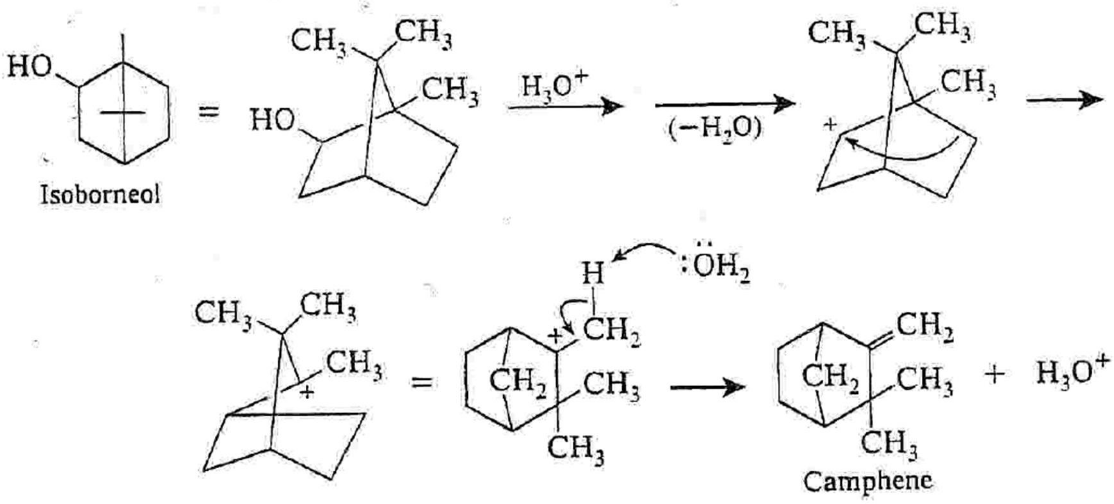


Problem 7.12

İzoborneol olarak adlandırılan bileşik %50'lik sülfürik asitle ısıtıldığında, bu tepkimenin ürünü, oluşması muhtemel olan bornilen değil, komfen olarak adlandırılan bileşiktir. Modelleri size yardımcı olarak kullanarak, kamfenin nasıl oluştuğunu gösteren bir mekanizmayı basamak basamak yazınız.



7.12

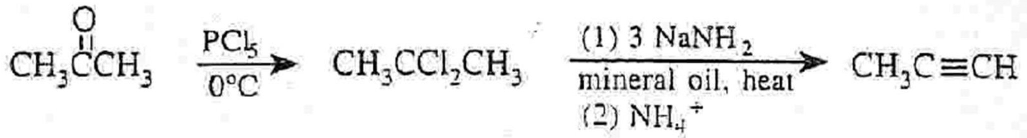


Problem 7.13

Propinin, aşağıdaki bileşiklerin her birinden sentezindeki tüm basamakları gösteriniz.

(a) CH_3COCH_3
(b) $CH_3CH_2CHBr_2$
(c) $CH_3CHBrCH_2Br$
(d) $CH_3CH{=}CH_2$

7.13 (a)

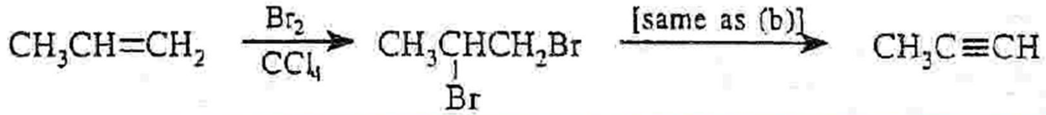


$$CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[0°C]{PCl_5} CH_3CCl_2CH_3 \xrightarrow[\substack{\text{mineral oil, heat}\\ (2)\ NH_4^+}]{(1)\ 3\ NaNH_2} CH_3C\equiv CH$$

(b) $$CH_3CH_2CHBr_2 \xrightarrow[\substack{\text{mineral oil, heat}\\ (2)\ NH_4^+}]{(1)\ 3\ NaNH_2} CH_3C\equiv CH$$

(c) $$CH_3CHBrCH_2Br \xrightarrow{\text{[same as (b)]}} CH_3C\equiv CH$$

(d)



$$CH_3CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} CH_3\underset{\underset{Br}{|}}{C}HCH_2Br \xrightarrow{\text{[same as (b)]}} CH_3C\equiv CH$$

Problem 7.14 ➤ Aşağıdaki asit-baz tepkimelerinin ürünlerini tahmin ediniz. Eğer dengede kayda değer miktarda ürün oluşmazsa, onu da belirtiniz. Her bir durumda, daha kuvvetli asidi, daha kuvvetli bazı, daha zayıf asidi ve daha zayıf bazı belirleyip işaretleyiniz.

(a) $CH_3CH{=}CH_2 + NaNH_2 \longrightarrow$

(b) $CH_3C\equiv CH + NaNH_2 \longrightarrow$

(c) $CH_3CH_2CH_3 + NaNH_2 \longrightarrow$

(d) $CH_3C\equiv C:^- + CH_3CH_2OH \longrightarrow$

(e) $CH_3C\equiv C:^- + NH_4Cl \longrightarrow$

7.14 (a) $$CH_3CH{=}CH_2 + NaNH_2 \longrightarrow \text{No reaction}$$

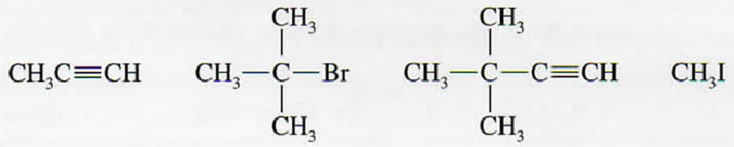
(b) $$\underset{\substack{\text{Stronger}\\ \text{acid}}}{CH_3C\equiv C{-}H} + \underset{\substack{\text{Stronger}\\ \text{base}}}{Na^+\ {}^-{:}\ddot{N}H_2} \longrightarrow \underset{\substack{\text{Weaker}\\ \text{base}}}{CH_3C\equiv C{:}^-\ Na^+} + \underset{\substack{\text{Weaker}\\ \text{acid}}}{:NH_3}$$

(c) $$CH_3CH_2CH_3 + NaNH_2 \longrightarrow \text{No reaction}$$

(d) $$\underset{\substack{\text{Stronger}\\ \text{base}}}{CH_3C\equiv C{:}^-} + \underset{\substack{\text{Stronger}\\ \text{acid}}}{H{-}\ddot{O}CH_2CH_3} \longrightarrow \underset{\substack{\text{Weaker}\\ \text{acid}}}{CH_3C\equiv CH} + \underset{\substack{\text{Weaker}\\ \text{base}}}{{}^-{:}\ddot{O}CH_2CH_3}$$

(e) $$\underset{\substack{\text{Stronger}\\ \text{base}}}{CH_3C\equiv C{:}^-} + \underset{\text{Stronger acid}}{H{-}\overset{+}{N}H_3} \longrightarrow \underset{\substack{\text{Weaker}\\ \text{acid}}}{CH_3C\equiv CH} + \underset{\substack{\text{Weaker}\\ \text{base}}}{:NH_3}$$

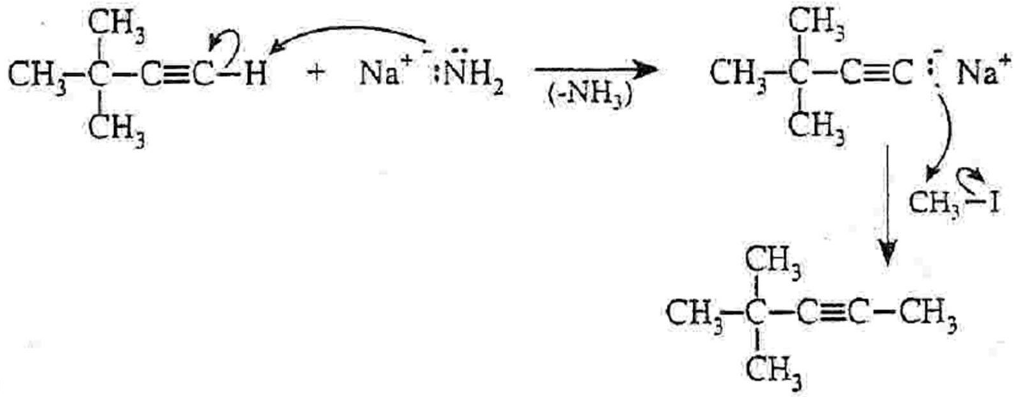
Amacınız, 4,4-dimetil-2-pentil sentezlemek olsun. Bunun için, aşağıdaki reaktiflerin herhangi birini seçerek başlayabilirsiniz. ⮜ **Problem 7.15**



$$CH_3C\equiv CH \qquad CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}Br \qquad CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}C\equiv CH \qquad CH_3I$$

Elinizde sodyum amit ve sıvı amonyağın da olduğunu varsayınız. İstenen bileşiğin en iyi sentezini tasarlayınız.

7.15



Problem 7.16

(a) 2-Heksenin hidrojen eksikliği indeksi nedir? (b) Metilsiklopentanın hidrojen eksikliği indeksi kaçtır? (c) Hidrojen eksikliği indeksi, zincirdeki ikili bağın konumu hakkında herhangi bir fikir verir mi? (d) Hidrojen eksikliği indeksi, halkanın büyüklüğü hakkında bir fikir verir mi? (e) 2-Heksinin hidrojen eksikliği indeksi kaçtır? (f) Genel anlamda $C_{10}H_{16}$ molekül formülüne sahip bir bileşik için hangi yapısal olasılıklar mümkündür?

7.16 (a) C_6H_{14} = formula of alkane
$\underline{C_6H_{12}}$ = formula of 2-hexene
H_2 = difference = 1 pair of hydrogen atoms

Index of hydrogen deficiency = 1

(b) C_6H_{14} = formula of alkane
$\underline{C_6H_{12}}$ = formula of methylcyclopentane
H_2 = difference = 1 pair of hydrogen atoms

Index of hydrogen deficiency = 1

(c) No, all isomers of C_6H_{12}, for example, have the same index of hydrogen deficiency.

(d) No

(e) C_6H_{14} = formula of alkane
$\underline{C_6H_{10}}$ = formula of 2-hexyne
H_4 = difference = 2 pairs of hydrogen atoms

Index of hydrogen deficiency = 2

(f) $C_{10}H_{22}$ (alkane)
$\underline{C_{10}H_{16}}$ (compound)
H_6 = difference = 3 pairs of hydrogen atoms

Index of hydrogen deficiency = 3

The structural possibilities are thus

3 double bonds
1 double bond and one triple bond
2 double bonds and 1 ring
1 double bond and 2 rings
3 rings
1 triple bond and one ring

Zencefilden izole edilen zingiberen güzel kokulu bir bileşiktir; $C_{15}H_{24}$ molekül formülüne sahiptir ve hiçbir üçlü bağ bulundurmadığı bilinmektedir. (a) Zingiberenin hidrojen eksikliği indeksi nedir? (b) Zingiberen, aşırı hidrojen kullanılarak katalitik hidrojenlemeye uğratıldığında, bir mol zingiberenin 3 mol hidrojen kattığı ve molekül formülü $C_{15}H_{30}$ olan bir bileşik oluşturduğu belirlenmiştir. Bir zingiberen molekülünde kaç tane ikili bağ vardır? (c) Bir zingiberen molekülünde kaç tane halka vardır?

◄ **Problem 7.17**

7.17 (a) $C_{15}H_{32}$ = formula of alkane
$\underline{C_{15}H_{24}}$ = formula of zingiberene
H_8 = difference = 4 pairs of hydrogen atoms

Index of hydrogen deficiency = 4

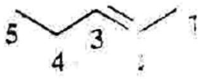
(b) Since 1 mol of zingiberene absorbs 3 mol of hydrogen, one molecule of zingiberene must contain three double bonds. (We are told that molecules of zingiberene do not contain any triple bonds.)

(c) If a molecule of zingiberene has three double bonds and an index of hydrogen deficiency equal to 4, it must have one ring. (The structural formula for zingiberene can be found in Problem 23.2.)

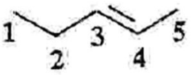
7.18 Aşağıdaki bileşiklerin adları doğru değildir. Doğru adı veriniz ve nedenini açıklayınız.

(a) *trans*-2-penten
(b) 1,1-Dimetileten
(c) 2-Metilsikloheksen
(d) 4-Metilsiklobüten
(e) (*Z*)-3-Kloro-2-büten
(f) 5,6-Diklorosikloheksen

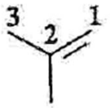
7.18 (a) We designate the position of the double bond by using the *lower* number of the two numbers of the doubly bonded carbon atoms, and the chain is numbered from the end nearer the double bond. The correct name is *trans*-2-pentene



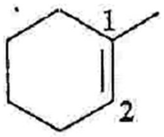
not



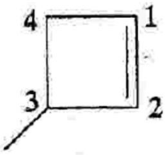
(b) We must choose the longest chain for the base name. The correct name is 2-methylpropene.



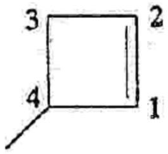
(c) We use the lower number of the two doubly bonded carbon atoms to designate the position of the double bond. The correct name is 1-methylcyclohexene.



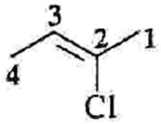
(d) We must number the ring starting with the double bond in the direction that gives the substituent the lower number. The correct name is 3-methylcyclobutene.



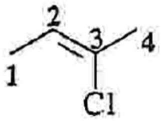
not



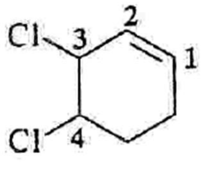
(e) We number in the way that gives the double bond *and the substituent* the lower number. The correct name is (Z)-2-chloro-2-butene.



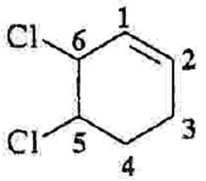
not



(f) We number the ring starting with the double bond so as to give the substituents the lower numbers. The correct name is 3,4-dichlorocyclohexene.



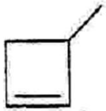
not



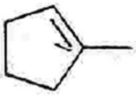
7.19 Aşağıdaki bileşiklerin yapı formüllerini yazınız:

- **(a)** 3-Metilsiklobüten
- **(b)** 1-Metilsiklopenten
- **(c)** 2,3-Dimetil-2-penten
- **(d)** (*Z*)-3-Heksen
- **(e)** (*E*)-2-Penten
- **(f)** 3,3,3-Tribromopropen
- **(g)** (*Z*,4*R*)-4-Metil-2-heksen
- **(h)** (*E*,4*S*)-4-Kloro-2-penten
- **(i)** (*Z*)-1-Siklopropil-1-penten
- **(j)** 5-Siklobütil-1-penten
- **(k)** (*R*)-4-Kloro-2-pentin
- **(l)** (*E*)-4-Metil-4-heksen-1-in

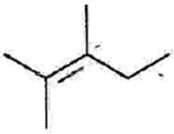
7.19 (a)



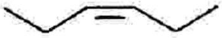
(b)



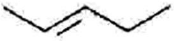
(c)



(d)

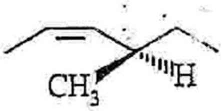


(e)

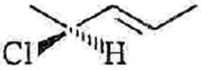


(f) $CH_2{=}CHCBr_3$

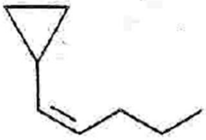
(g)



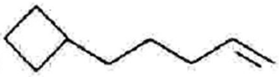
(h)



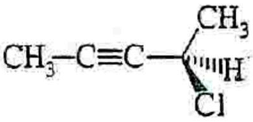
(i)



(j)

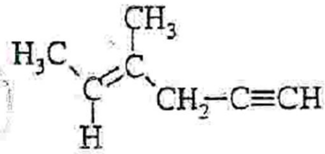


(k)



$CH_3{-}C{\equiv}C{-}C(CH_3)(H)(Cl)$

(l)

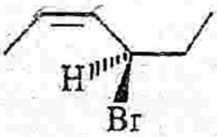


$H_3C{-}CH{=}C(CH_3){-}CH_2{-}C{\equiv}CH$

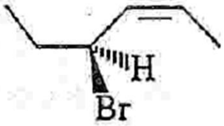
7.20 Aşağıdaki bileşiklerin üç boyutlu formüllerini yazınız ve bu izomerleri (*R*–*S*) ve (*E*)–(*Z*) adlandırma sistemiyle adlandırınız.

- **(a)** 4-Bromo-2-heksen
- **(b)** 3-Kloro-1,4-heksadien
- **(c)** 2,4-Dikloro-2-penten
- **(d)** 2-Bromo-4-kloro-2-heksen-5-in

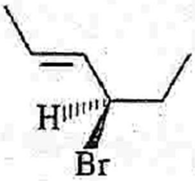
7.20 (a)



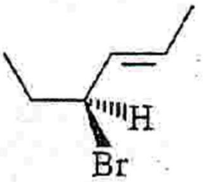
(*Z*,4*R*)-4-Bromo-2-hexene



(*Z*,4*S*)-4-Bromo-2-hexene

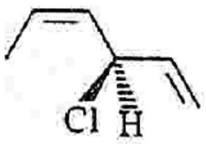


(*E*,4*R*)-4-Bromo-2-hexene

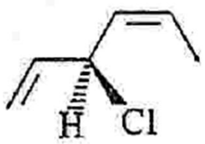


(*E*,4*S*)-4-Bromo-2-hexene

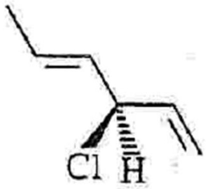
(b)



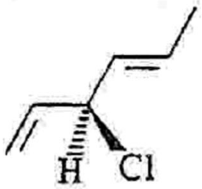
(*3R,4Z*)-3-Chloro-1,4-hexadiene



(*3S,4Z*)-3-Chloro-1,4-hexadiene

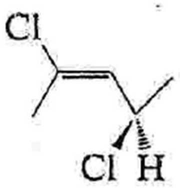


(*3R,4E*)-3-Chloro-1,4-hexadiene

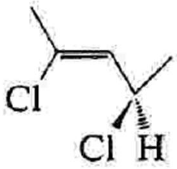


(*3S,4E*)-3-Chloro-1,4-hexadiene

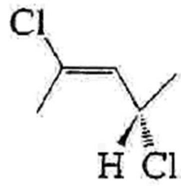
(c)



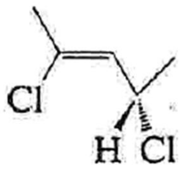
(*2E,4R*)-2,4-Dichloro-2-pentene



(*2Z,4R*)-2,4-Dichloro-2-pentene

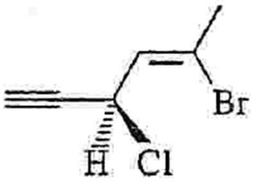


(*2E,4S*)-2,4-Dichloro-2-pentene

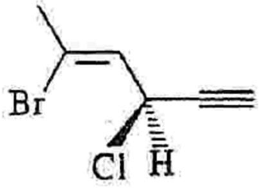


(*2Z,4S*)-2,4-Dichloro-2-pentene

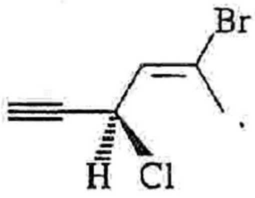
(d)



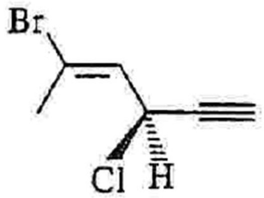
(*3R,4Z*)-5-Bromo-3-chloro-4-hexen-1-yne



(*3S,4Z*)-5-Bromo-3-chloro-4-hexen-1-yne



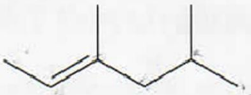
(*3R,4E*)-5-Bromo-3-chloro-4-hexen-1-yne



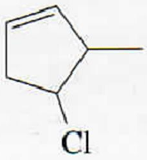
(*3S,4E*)-5-Bromo-3-chloro-4-hexen-1-yne

7.21 Aşağıdaki bileşiklerin her birinin IUPAC adlarını yazınız.

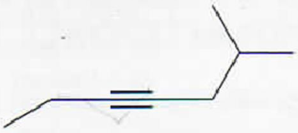
(a)



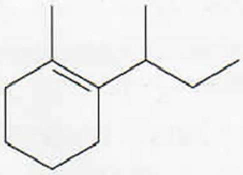
(b)



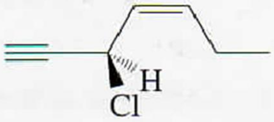
(c)



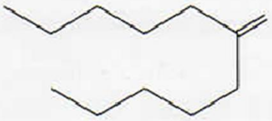
(d)



(e)



(f)



7.21 (a) (*E*)-3,5-Dimethyl-2-hexene

(b) 4-Chloro-3-methylcyclopentene

(c) 6-Methyl-3-heptyne

(d) 1-*sec*-Butyl-2-methylcyclohexene or 1-methyl-2-(1-methylpropyl)cyclohexene

(e) (*Z*,3*R*)-3-Chloro-4-hepten-1-yne

(f) 2-Pentyl-1-heptene

7.22 Aşağıdaki maddelerin her birinden çıkarak propeni sentezleyiniz.

(a) Propil klorür

(b) İzopropil klorür

(c) Propil alkol

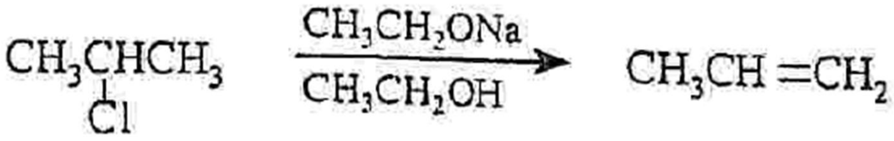
(d) İzopropil alkol

(e) 1,2-Dibromopropan

(f) Propin

7.22 (a) $CH_3CH_2CH_2Cl \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_3CH{=}CH_2$

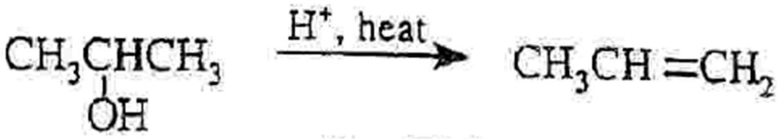
(b)



$CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3 \xrightarrow[CH_3CH_2OH]{CH_3CH_2ONa} CH_3CH{=}CH_2$

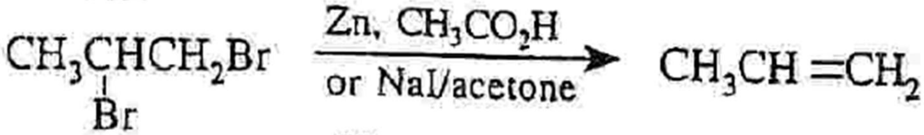
(c) $CH_3CH_2CH_2OH \xrightarrow{H^+,\ heat} CH_3CH{=}CH_2$

(d)



$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow{H^+,\ heat} CH_3CH{=}CH_2$

(e)



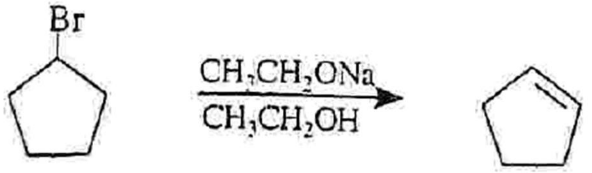
$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_2Br \xrightarrow[or\ NaI/acetone]{Zn,\ CH_3CO_2H} CH_3CH{=}CH_2$

(f) $CH_3C{\equiv}CH \xrightarrow[Ni_2B\ (P\text{-}2)]{H_2} CH_3CH{=}CH_2$

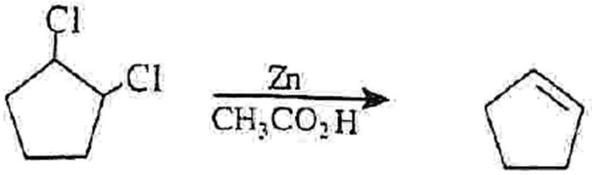
7.23 Aşağıdaki her bir bileşikten çıkarak siklopenteni sentezleyiniz.

(a) Bromosiklopentan, **(b)** 1,2-Diklorosiklopentan, **(c)** Siklopentanol

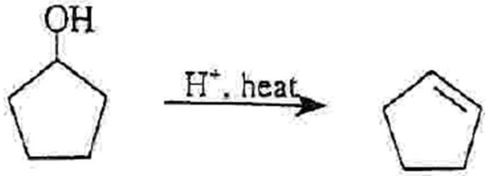
7.23 (a)



(b)

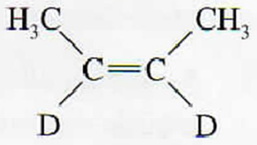


(c)



7.24 Etinden başlayarak aşağıdakilerden her birinin sentezini yazınız. Gerekli reaktifleri kullanabilirsiniz ve bu problemin daha önceki kısımlarında hazırlanan bileşiklerin sentezini göstermeniz gerekli değildir.

(a) Propin
(b) 1-Bütin
(c) 2-Bütin
(d) *cis*-2-Büten
(e) *trans*-2-Büten
(f) 1-Pentin
(g) 2-Heksin
(h) (*Z*)-2-Heksen
(i) (*E*)-2-Heksen
(j) 3-Heksin
(k) $CH_3CH_2C\equiv CD$
(l)

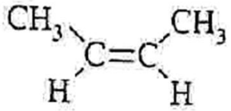


7.24 (a) $HC\equiv CH \xrightarrow[\text{liq. } NH_3]{NaNH_2} HC\equiv C:^- Na^+ \xrightarrow[(-NaI)]{CH_3-I} HC\equiv C-CH_3$

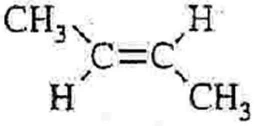
(b) $HC\equiv CH \xrightarrow[\text{liq. } NH_3]{NaNH_2} HC\equiv C:^- Na^+ \xrightarrow[(-NaBr)]{CH_3CH_2-Br} HC\equiv C-CH_2CH_3$

(c) $CH_3C\equiv CH \xrightarrow[\text{liq. } NH_3]{NaNH_2} CH_3C\equiv C:^- Na^+ \xrightarrow[(-NaI)]{CH_3-I} CH_3-C\equiv C-CH_3$
[from(a)]

(d) $CH_3-C\equiv C-CH_3 \xrightarrow[Ni_2B\ (P\text{-}2)]{H_2}$
[from(c)]

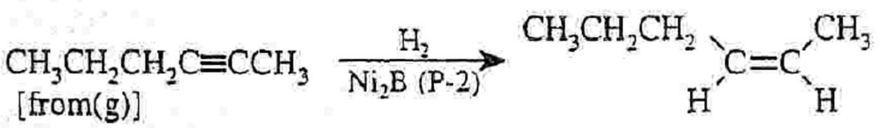


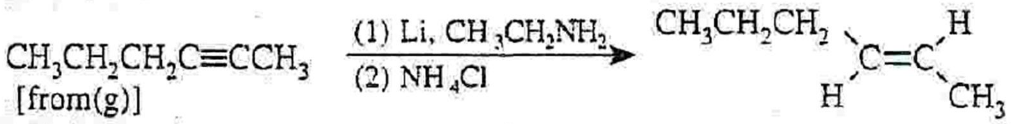
(e) $CH_3-C\equiv C-CH_3 \xrightarrow[(2)\ NH_4Cl]{(1)\ Li,\ CH_3CH_2NH_2}$
[from(c)]

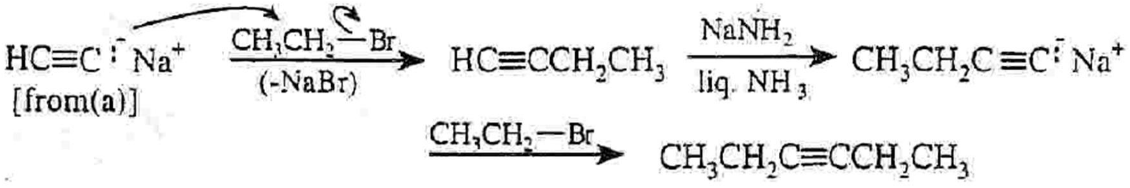


(f) $HC\equiv C:^- Na^+ \xrightarrow[(-NaBr)]{CH_3CH_2CH_2-Br} HC\equiv C-CH_2CH_2CH_3$
[from(a)]

(g) $CH_3CH_2CH_2C\equiv CH \xrightarrow[\text{liq. } NH_3]{NaNH_2} CH_3CH_2CH_2C\equiv C:^- Na^+ \xrightarrow[(-NaI)]{CH_3-I} CH_3CH_2CH_2C\equiv CCH_3$
[from(f)]

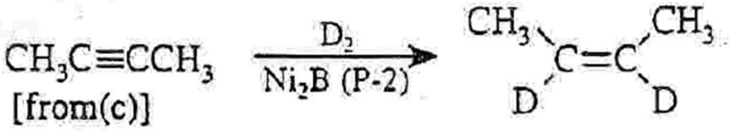
(h) 

(i) 

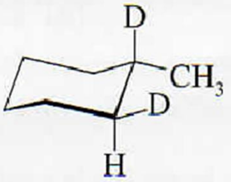
(j) 

(k) $CH_3CH_2C\equiv C:^- Na^+ \xrightarrow{D_2O} CH_3CH_2C\equiv CD$

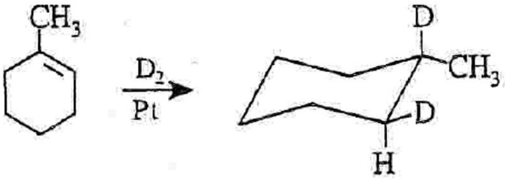
[from(j)]

(l) 

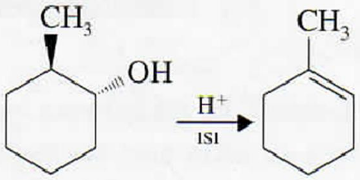
7.25 1-Metilsikloheksenle başlayarak ve herhangi diğer gerekli reaktifleri kullanarak, aşağıdaki döteryum etiketli bileşiğin sentezini tasarlayınız.



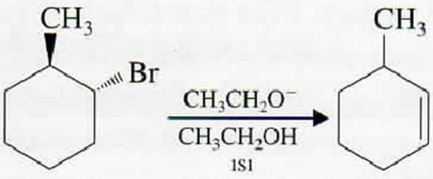
7.25 We notice that the deuterium atoms are cis to each other, and we conclude, therefore, that we need to choose a method that will cause a syn addition of deuterium. One way would be to use D_2 and a metal catalyst (Section 7.13)



7.26 *trans*-2-Metilsikloheksanolden asit katalizli su çıkartıldığında (bkz. aşağıdaki tepkime), ana ürün 1-metilsikloheksendir:

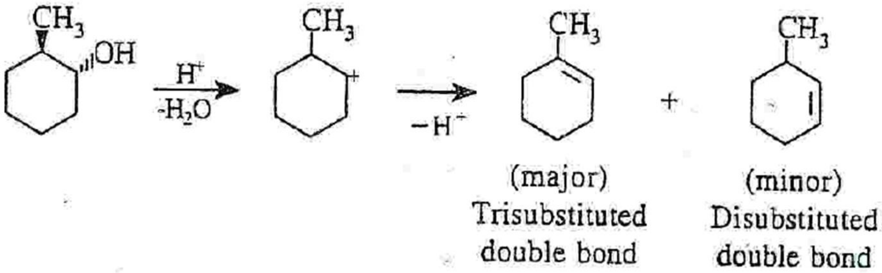


Ancak, *trans*-1-bromo-2-metilsikloheksandan hidrojen halojenür çıkartıldığında ise ana ürün 3-metilsikloheksendir:

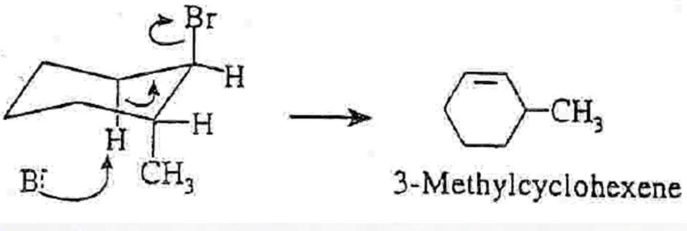


Bu iki tepkimenin değişik ürünler vermesinin nedenini açıklayınız.

7.26 Dehydration of *trans*-2-methylcyclohexanol proceeds through the formation of a carbocation (through an E1 reaction of the protonated alcohol) and leads preferentially to the more stable alkene. 1-Methylcyclohexene (below) is more stable than 3-methylcyclohexene (the minor product of the dehydration) because its double bond is more highly substituted.



Dehydrohalogenation of *trans*-1-bromo-2-methylcyclohexane is an E2 reaction and must proceed through an anti periplanar transition state. Such a transition state is possible only for the elimination leading to 3-methylcyclohexene (cf. Problem 7.8).



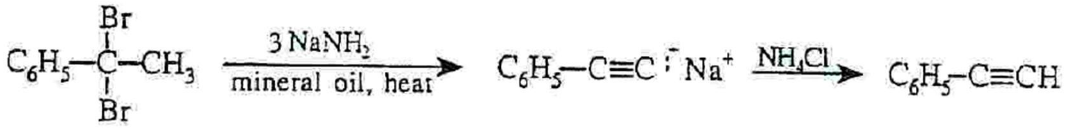
7.27 Aşağıdakilerin her birinden feniletin sentezleyiniz.

(a) 1,1-Dibromo-1-feniletan

(b) 1,1-Dibromo-2-feniletan

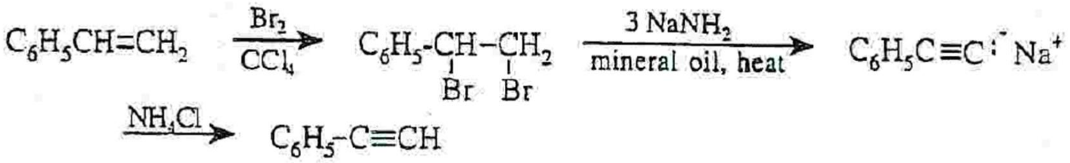
(c) Fenileten (stiren)

(d) Asetofenon ($C_6H_5COCH_3$)

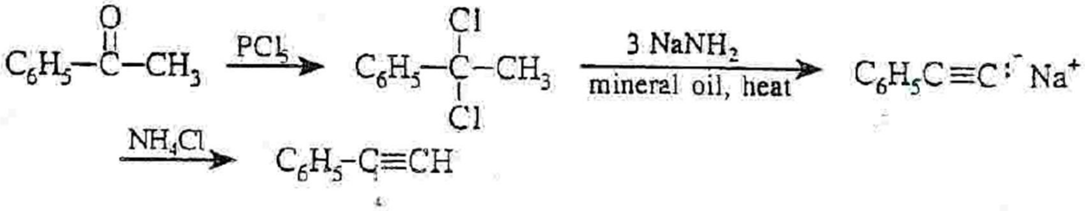
7.27 (a) 

$$C_6H_5-\overset{Br}{\underset{Br}{C}}-CH_3 \xrightarrow[\text{mineral oil, heat}]{3\,NaNH_2} C_6H_5-C\equiv C\colon^- Na^+ \xrightarrow{NH_4Cl} C_6H_5-C\equiv CH$$

(b) $C_6H_5CH_2-CHBr_2 \xrightarrow[\text{mineral oil, heat}]{3\,NaNH_2} C_6H_5C\equiv C\colon^- Na^+ \xrightarrow{NH_4Cl} C_6H_5-C\equiv CH$

(c) 

$$C_6H_5CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} C_6H_5\text{-}\underset{Br}{CH}-\underset{Br}{CH_2} \xrightarrow[\text{mineral oil, heat}]{3\,NaNH_2} C_6H_5C\equiv C\colon^- Na^+ \xrightarrow{NH_4Cl} C_6H_5-C\equiv CH$$

(d) 

$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{PCl_5} C_6H_5-\overset{Cl}{\underset{Cl}{C}}-CH_3 \xrightarrow[\text{mineral oil, heat}]{3\,NaNH_2} C_6H_5C\equiv C\colon^- Na^+ \xrightarrow{NH_4Cl} C_6H_5-C\equiv CH$$

7.28 Siklobütanın yanma ısısı 2744 kJ mol^{-1}'dir. Bu, bütenin izomerleriyle karşılaştırıldığında siklobütanın bağıl kararlılığı hakkında ne anlama gelir (Altbölüm 7.3B)?

7.28 Cyclobutane is less stable than any of the butene isomers.

7.29 Verilen yanma ısılarını (3375 kJ mol^{-1}, 3369 kJ mol^{-1}, 3365 kJ mol^{-1}, 3361 kJ mol^{-1}, 3355 kJ mol^{-1}) aşağıdaki alkenlerle karşılaştırınız: *cis*-2-Penten, *trans*-2-penten, 2-metil-2-büten, 1-penten, 2-metil-1-büten. Yanma ısıları hangi alkenlere karşılık gelmektedir?

7.29 1-Pentene, 3375 kJ mol^{-1}

cis-2-Pentene, 3369 kJ mol^{-1}

trans-2-Pentene, 3365 kJ mol^{-1}

2-Methyl-1-butene, 3361 kJ mol^{-1}

2-Methyl-2-butene, 3355 kJ mol^{-1}

7.30 Çizelgelere bakmasızın, aşağıdaki bileşikleri azalan asitlik derecelerine göre düzenleyiniz.

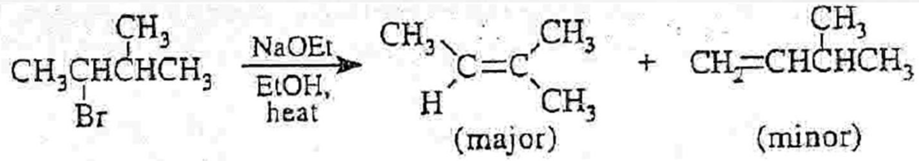
pentan 1-penten 1-pentin 1-pentanol

7.30 1-Pentanol > 1-pentyne > 1-pentene > pentane
(See Section 3.7 for the explanation.)

7.31 Aşağıdaki alkil halojenürlerin her birinin etanol içerisinde sodyum etoksitle ısıtılması sonucu elde edilen tüm ürünlerin yapı formüllerini yazınız. Birden daha fazla ürün oluştuğunda, hangisinin ana ürün ve hangisinin yan ürün (ürünler) olduğunu gösteriniz. Bu soruyu cevaplarken, bu ürünlerin cis–trans izomerlerini ihmal edebilirsiniz.

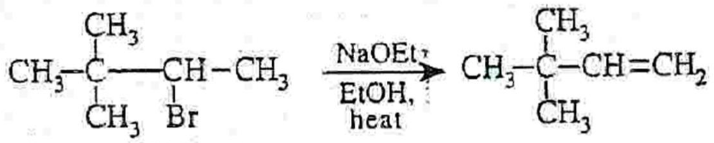
(a) 2-Bromo-3-metilbütan
(b) 3-Bromo-2,2-dimetilbütan
(c) 3-Bromo-3-metilpentan
(d) 1-Bromo-1-metilsikloheksan
(e) *cis*-1-Bromo-2-etilsikloheksan
(f) *trans*-1-Bromo-2-etilsikloheksan

7.31 (a)



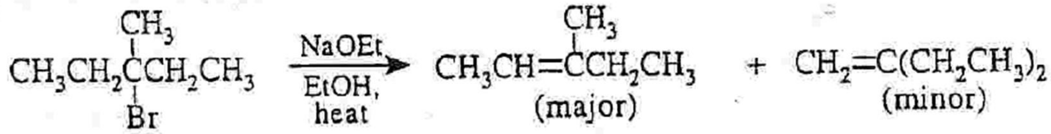
$$CH_3\underset{Br}{CH}\overset{CH_3}{CH}CH_3 \xrightarrow[\text{EtOH, heat}]{\text{NaOEt}} \underset{\text{(major)}}{(CH_3)(H)C{=}C(CH_3)_2} + \underset{\text{(minor)}}{CH_2{=}CH\overset{CH_3}{CH}CH_3}$$

(b)



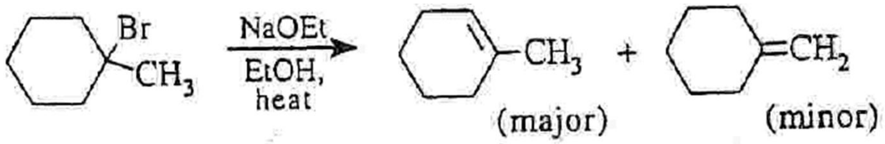
$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{Br}{CH}{-}CH_3 \xrightarrow[\text{EtOH, heat}]{\text{NaOEt}} CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH{=}CH_2$$

(c)

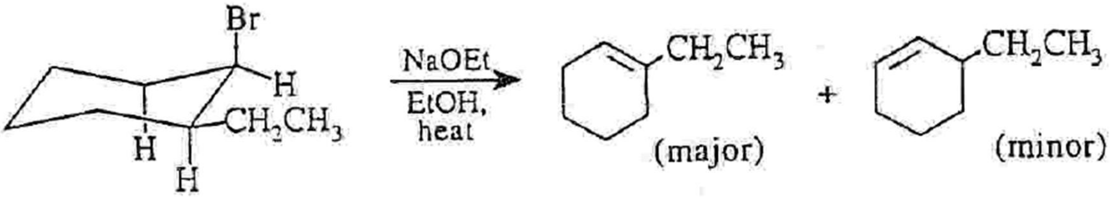


$$CH_3CH_2\underset{Br}{\overset{CH_3}{C}}CH_2CH_3 \xrightarrow[\text{EtOH, heat}]{\text{NaOEt}} \underset{\text{(major)}}{CH_3CH{=}\overset{CH_3}{C}CH_2CH_3} + \underset{\text{(minor)}}{CH_2{=}C(CH_2CH_3)_2}$$

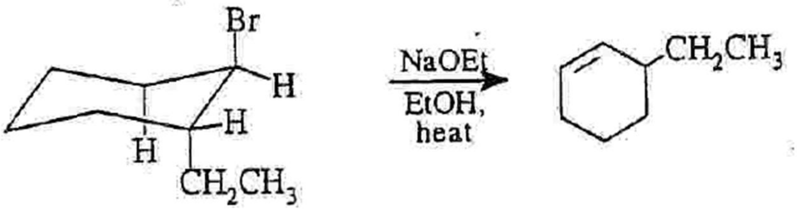
(d)



(e)



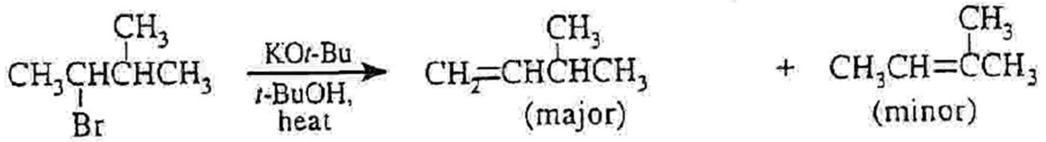
(f)



7.32 Aşağıdaki alkil halojenürlerin her birinin, *ter*-bütil alkol içinde potasyum *ter*-bütoksitle ısıtılması sonucu elde edilen ürünlerin yapı formüllerini yazınız Birden daha fazla ürün oluştuğunda, hangisinin ana ürün ve hangisinin yan ürün (ürünler) olduğunu gösteriniz. Bu soruyu cevaplarken, bu ürünlerin cis–trans izomerlerini ihmal edebilirsiniz.

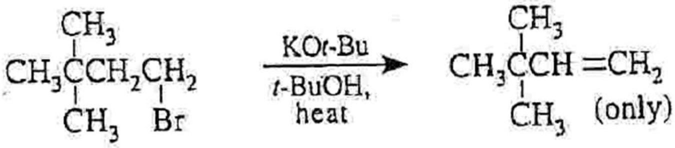
(a) 2-Bromo-3-metilbütan
(b) 4-Bromo-2,2-dimetilbütan
(c) 3-Bromo-3-metilpentan
(d) 4-Bromo-2,2-dimetilpentan
(e) 1-Bromo-1-metilsikloheksan

7.32 (a)



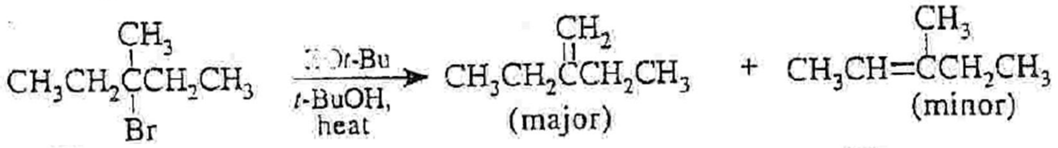
$$CH_3\underset{Br}{C}H\overset{CH_3}{C}HCH_3 \xrightarrow[t\text{-BuOH, heat}]{KOt\text{-Bu}} CH_2{=}CH\overset{CH_3}{C}HCH_3\ (\text{major}) + CH_3CH{=}\overset{CH_3}{C}CH_3\ (\text{minor})$$

(b)



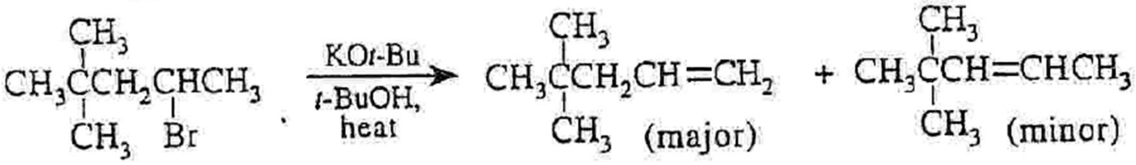
$$CH_3\underset{CH_3}{\overset{CH_3}{C}}CH_2\underset{Br}{C}H_2 \xrightarrow[t\text{-BuOH, heat}]{KOt\text{-Bu}} CH_3\underset{CH_3}{\overset{CH_3}{C}}CH{=}CH_2\ (\text{only})$$

(c)



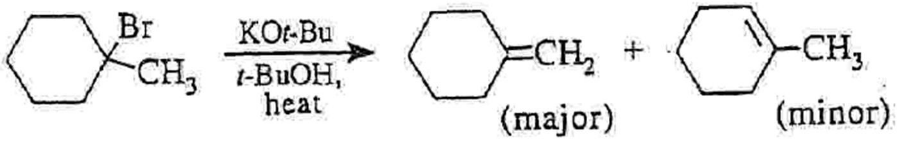
$$CH_3CH_2\underset{Br}{\overset{CH_3}{C}}CH_2CH_3 \xrightarrow[t\text{-BuOH, heat}]{KOt\text{-Bu}} CH_3CH_2\overset{CH_2}{\overset{\|}{C}}CH_2CH_3\ (\text{major}) + CH_3CH{=}\overset{CH_3}{C}CH_2CH_3\ (\text{minor})$$

(d)



$$CH_3\underset{CH_3}{\overset{CH_3}{C}}CH_2\underset{Br}{C}HCH_3 \xrightarrow[t\text{-BuOH, heat}]{KOt\text{-Bu}} CH_3\underset{CH_3}{\overset{CH_3}{C}}CH_2CH{=}CH_2\ (\text{major}) + CH_3\underset{CH_3}{\overset{CH_3}{C}}CH{=}CHCH_3\ (\text{minor})$$

(e)

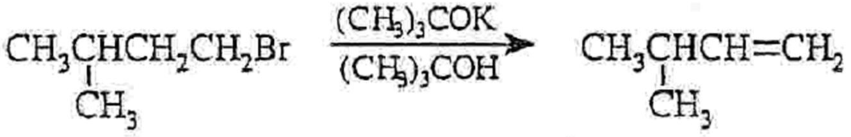


7.33 Bir uygun alkil halojenür ve bazla başlayarak, aşağıdaki alkenleri ana (veya tek) ürün olarak oluşturan sentezleri tasarlayınız.

(a) 1-Penten	**(d)** 4-Metilsikloheksen
(b) 3-Metil-1-büten	**(e)** 1-Metilsiklopenten
(c) 2,3-Dimetil-1-büten	

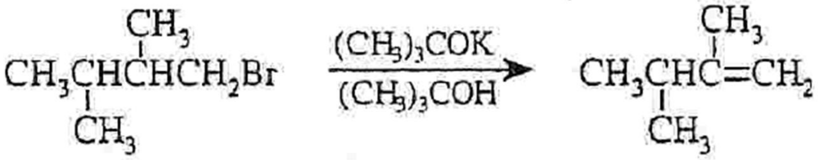
7.33 (a) $CH_3CH_2CH_2CH_2CH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_3CH_2CH_2CH{=}CH_2$

(b)



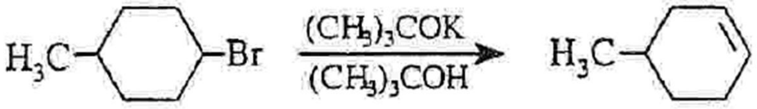
$$CH_3\underset{CH_3}{C}HCH_2CH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_3\underset{CH_3}{C}HCH{=}CH_2$$

(c)

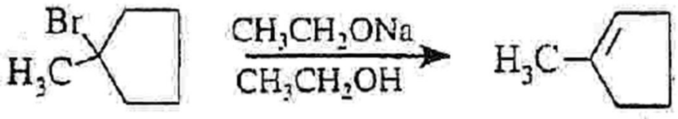


$$CH_3\underset{CH_3}{C}H\overset{CH_3}{C}HCH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_3\underset{CH_3}{C}H\overset{CH_3}{C}{=}CH_2$$

(d)



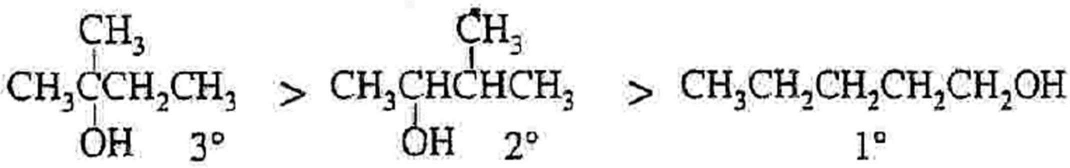
(e)



7.34 Aşağıdaki alkolleri asit katalizli su çıkarılması tepkimelerindeki etkinlik sırasına göre düzenleyiniz (Önce en etkin olandan başlayınız).

1-pentanol 2-metil-2-bütanol 3-metil-2-bütanol

7.34

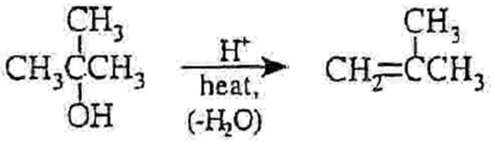


$$CH_3\overset{CH_3}{\underset{OH}{C}}CH_2CH_3 \;\; 3° > CH_3\underset{OH}{C}H\overset{CH_3}{C}HCH_3 \;\; 2° > CH_3CH_2CH_2CH_2CH_2OH \;\; 1°$$

7.35 Aşağıdaki alkollerin her biri asit katalizli su çıkartılması tepkimesine uğratıldığında oluşan ürünleri yazınız. Eğer birden fazla ürün oluşursa, ana ürün olan alkeni gösteriniz (cis–trans izomerisini ihmal ediniz).

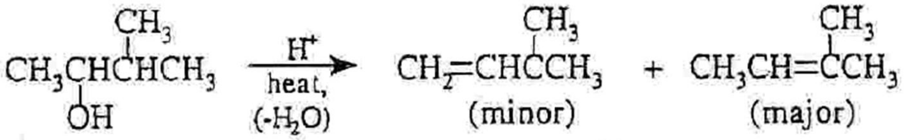
(a) 2-Metil-2-propanol
(b) 3-Metil-2-bütanol
(c) 3-Metil-3-pentanol
(d) 2,2-Dimetil-1-propanol
(e) 1,4-Dimetilsikloheksanol

7.35 (a)



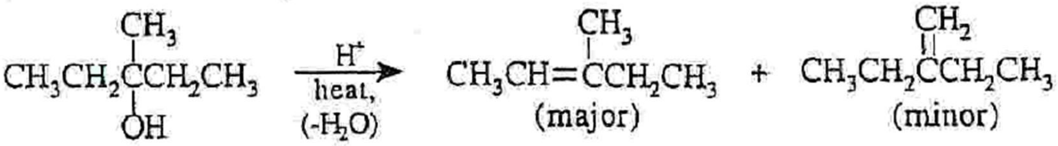
$$CH_3\overset{CH_3}{\underset{OH}{C}}CH_3 \xrightarrow[\substack{\text{heat,}\\(-H_2O)}]{H^+} CH_2{=}\overset{CH_3}{C}CH_3$$

(b)



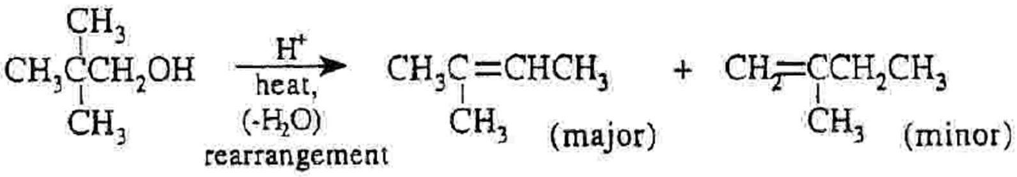
$$CH_3\underset{OH}{C}H\overset{CH_3}{C}HCH_3 \xrightarrow[\substack{\text{heat,}\\(-H_2O)}]{H^+} \underset{\text{(minor)}}{CH_2{=}CH\overset{CH_3}{C}CH_3} + \underset{\text{(major)}}{CH_3CH{=}\overset{CH_3}{C}CH_3}$$

(c)



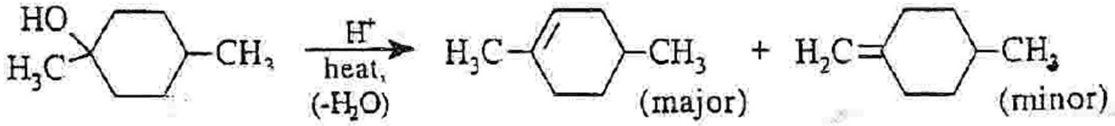
$$CH_3CH_2\overset{CH_3}{\underset{OH}{C}}CH_2CH_3 \xrightarrow[\substack{\text{heat,}\\(-H_2O)}]{H^+} \underset{\text{(major)}}{CH_3CH{=}\overset{CH_3}{C}CH_2CH_3} + \underset{\text{(minor)}}{CH_3CH_2\overset{CH_2}{\overset{\|}{C}}CH_2CH_3}$$

(d)

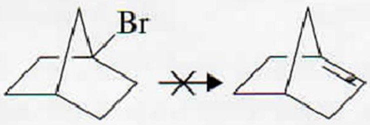


$$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2OH \xrightarrow[\substack{\text{heat,}\\(-H_2O)\\\text{rearrangement}}]{H^+} CH_3\underset{CH_3}{C}{=}CHCH_3 \text{ (major)} + CH_2{=}\underset{CH_3}{C}CH_2CH_3 \text{ (minor)}$$

(e)

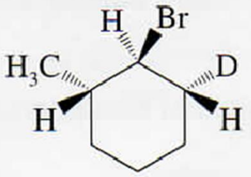


7.36 1-Bromobisiklo[2,2,1]heptan, bazla ısıtıldığında ayrılma tepkimesine (aşağıda) uğramaz. Tepkimeyi engelleyen olumsuzluğu açıklayınız. (Molekül modelleri kullanmanızın yardımı olabilir.)

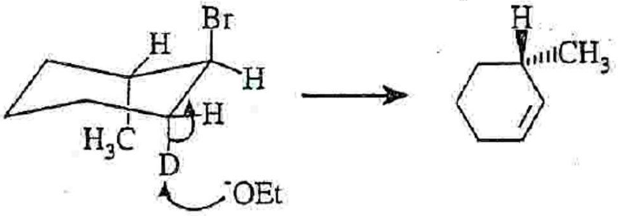


7.36 The alkene cannot be formed because the double bond in the product is too highly strained. Recall that the atoms at each carbon of a double bond prefer to be in the same plane.

7.37 Aşağıda gösterilen döteryum etiketli bileşik, etanol içerisinde sodyum etoksit kullanılarak hidrojen halojenür çıkarılması tepkimesine uğratıldığında, alken ürünü yalnızca 3-metilsikloheksendir. (Ürün, döteryum içermez.) Sonuç için bir açıklama yapınız.



7.37 Only the deuterium atom can assume the anti periplanar orientation necessary for an E2 reaction to occur.



7.38 Aşağıdaki olayların her biri için, mekanizmalarıyla birlikte, açıklamalar yapınız.

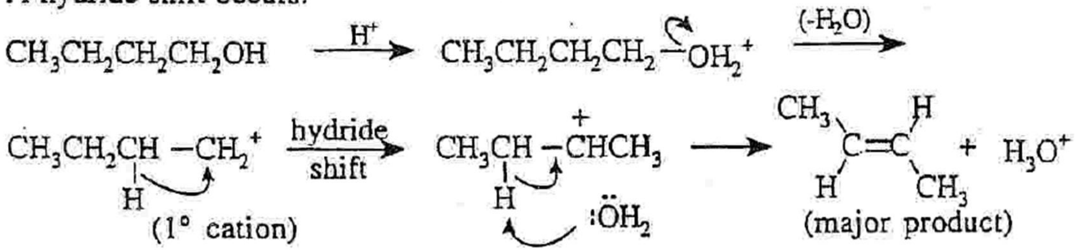
(a) 1-Bütanolün asit katalizli su çıkarılması tepkimesi ana ürün olarak *trans*-2-büten oluşturur.

(b) 2,2-Dimetilsikloheksanolün asit katalizli su çıkarılması tepkimesi ana ürün olarak 1,2-dimetilsikloheksen oluşturur.

(c) 3-İyodo-2,2-dimetilbütan, etanol içinde gümüş nitratla etkileştirildiğinde ana ürün olarak 2,3-dimetil-2-büten oluşturur.

(d) (1*S*, 2*R*)-1-Bromo-1,2-difenilpropandan hidrojen halojenür çıkartıldığında yalnızca (*E*)-1,2-difenilpropen oluşur.

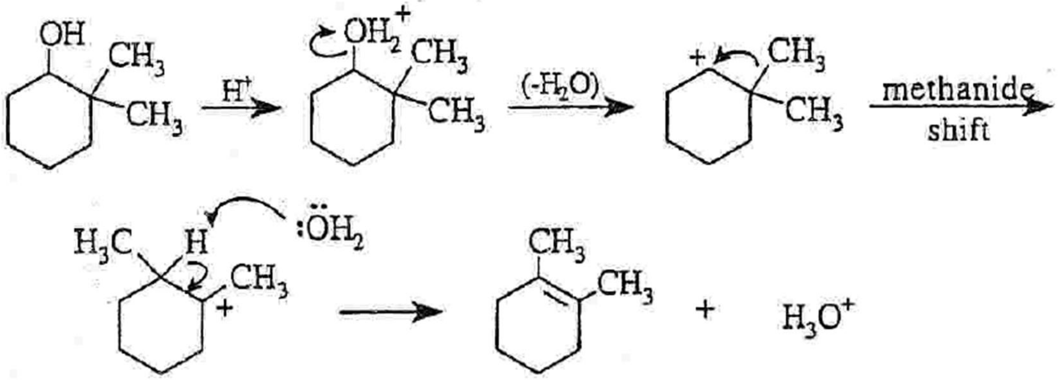
7.38 (a) A hydride shift occurs.



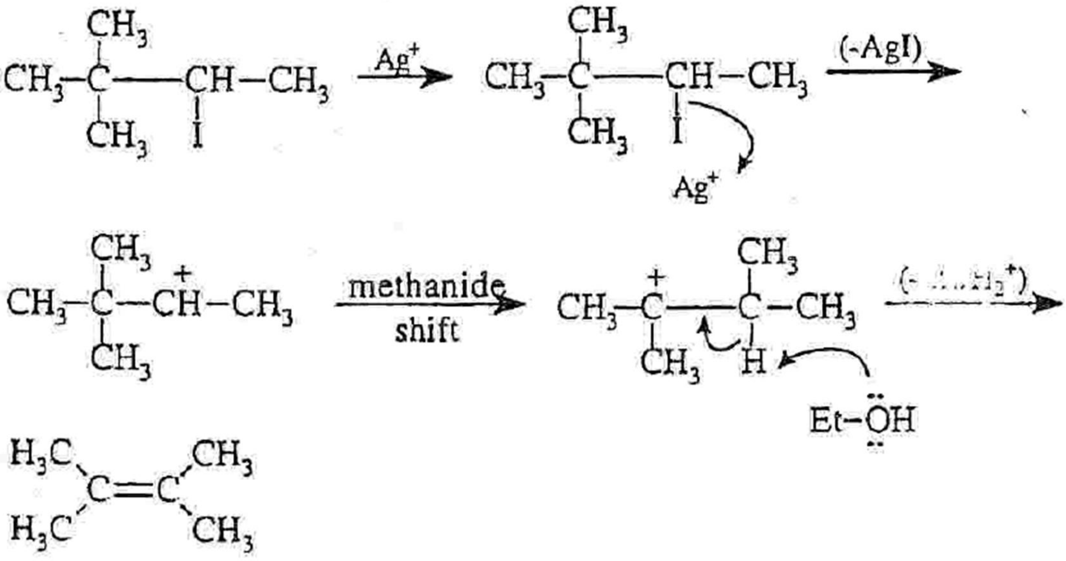
$$CH_3CH_2CH_2CH_2OH \xrightarrow{H^+} CH_3CH_2CH_2CH_2{-}OH_2^+ \xrightarrow{(-H_2O)}$$

$$CH_3CH_2\underset{H}{C}H{-}CH_2^+ \xrightarrow[\text{shift}]{\text{hydride}} CH_3\underset{H}{C}H{-}\overset{+}{C}HCH_3 \longrightarrow CH_3(H)C{=}C(H)CH_3 + H_3O^+$$

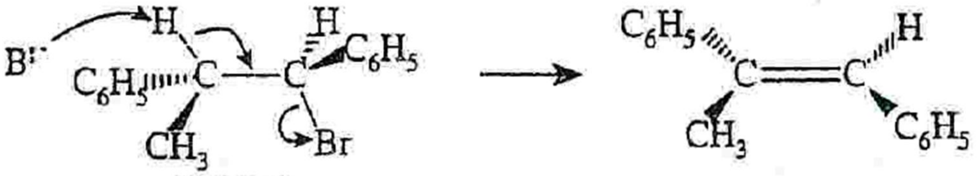
(b) A methanide shift occurs.



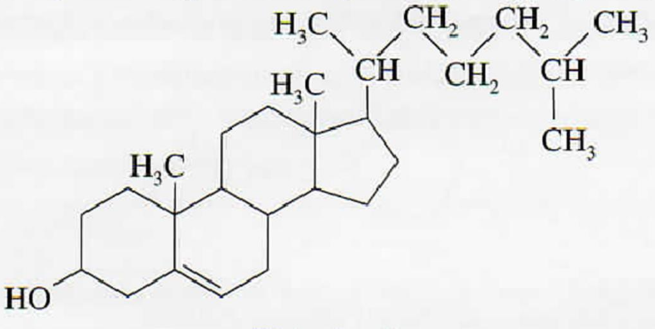
(c) A methanide shift occurs.



(d) The required anti periplanar transtition state leads only to (*E*) alkene:

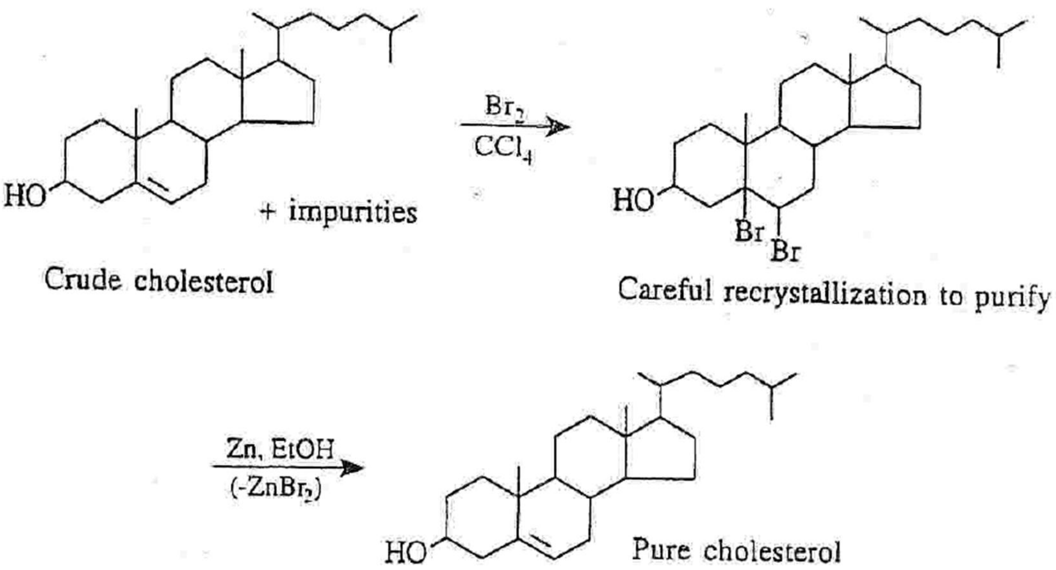


7.39 Kolesterol önemli bir steroittir ve yaklaşık olarak tüm vücut dokularında bulunur. Bu bileşik aynı zamanda safra taşlarının da önemli bileşenidir. Saf olmayan kolesterol, safra taşlarından bir organik çözücüyle özütlenerek elde edilebilir. Bundan dolayı, saf olmayan kolesterolün saflaştırılması için **(a)** CCl_4 içinde Br_2 ile etkileştirilir, **(b)** ürün dikkatlice kristallendirilir ve **(c)** daha sonra etanol içinde metalik çinkoyla etkileştirilir. Bu yöntem, hangi tepkimeleri içermektedir?



Kolesterol

7.39 In the first step, cholesterol reacts with bromine to form the *vic*-dibromide. This product is then purified by crystallization, and then treatment with zinc in ethanol converts the pure *vic*-dibromide back to cholesterol. (Recrystallization of the *vic*-dibromide is especially easy because it has a higher melting point than cholesterol.)



7.40 Karyofillen, karanfil çiçeği yağında bulunan bir bileşiktir, $C_{15}H_{24}$ molekül formülüne sahiptir ve üçlü bağ içermez. Karyofillenin, platin katalizörlüğünde aşırı hidrojenle tepkimesi $C_{15}H_{28}$ formülüne sahip bileşiği oluşturur. Bir karyofillen molekülünde **(a)** kaç tane ikili bağ ve **(b)** kaç tane halka bulunmaktadır?

7.40 (a) Caryophyllene has the same molecular formula as zingiberene (Problem 7.17); thus it, too, has an index of hydrogen deficiency equal to 4. That 1 mol of caryophyllene absorbs 2 mol of hydrogen on catalytic hydrogenation indicates the presence of two double bonds per molecule.

(b) Caryophyllene molecules must also have two rings. (See Problem 23.2 for the structure of caryophyllene.)

7.41 Skualen, steroitlerin biyosentezinde önemli bir bileşiktir, $C_{30}H_{50}$ formülüne sahiptir ve üçlü bağ içermez. **(a)** Skualenin hidrojen eksikliği indeksini bulunuz. **(b)** Skualen, katalitik hidrojenlemeye uğrayarak, $C_{30}H_{62}$ molekül formülüne sahip bir bileşik oluşturur. Bir skualen molekülünde kaç tane ikili bağ vardır? **(c)** Kaç tane halka vardır?

7.41 (a) $C_{30}H_{62}$ = formula of alkane

$\underline{C_{30}H_{50}}$ = formula of squalene

H_{12} = difference = 6 pairs of hydrogen atoms

Index of hydrogen deficiency = 6

(b) Molecules of squalene contain six double bonds.

(c) Squalene molecules contain no rings. (See Problem 23.2 for the structural formula of squalene.)

7.42 *cis*-2-Büten ve *trans*-2-bütenin birbirine dönüşümlerini düşününüz. **(a)** *cis*-2-Büten ⟶ *trans*-2-büten tepkimesinin $\Delta H°$ değeri nedir? **(b)** $\Delta H° \cong \Delta G°$ olduğunu varsayınız. Bu tepkime için hangi minimum $\Delta G^{\ddagger}$ değerini beklersiniz? **(c)** Bu tepkime için bir serbest enerji diyagramı taslağı çizerek, $\Delta G°$ ve $\Delta G^{\ddagger}$ 'leri belirtiniz.

7.42 (a) We are given (Section 7.3A) the following heats of hydrogenation:

$$\text{cis-2-Butene} + H_2 \xrightarrow{Pt} \text{butane} \qquad \Delta H^\circ = -120 \text{ kJ mol}^{-1}$$

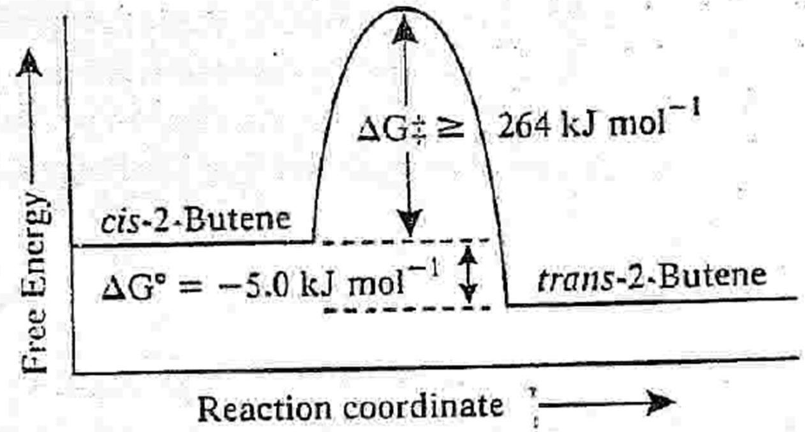
$$\text{trans-2-Butene} + H_2 \xrightarrow{Pt} \text{butane} \qquad \Delta H^\circ = -115 \text{ kJ mol}^{-1}$$

Thus, for

$$\text{cis-2-Butene} \longrightarrow \text{trans-2-butene} \qquad \Delta H^\circ = -5.0 \text{ kJ mol}^{-1}$$

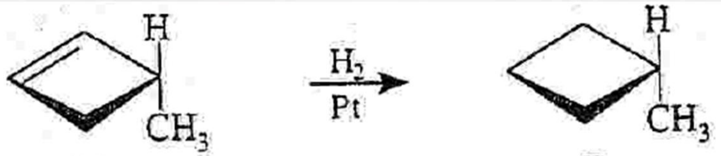
(b) Converting *cis*-2-butene into *trans*-2-butene involves breaking the π bond. Therefore, we would expect the energy of activation to be at least as large as the π-bond strength, that is, at least 264 kJ mol^{-1}.

(c)



7.43 **E–H** bileşikleri için yapılar öneriniz. **E** bileşiği, C_5H_8 molekül formülüne sahiptir ve optikçe aktiftir. Katalitik hidrojenlemeyle **E** bileşiği **F**'yi oluşturmaktadır. **F** bileşiği, C_5H_{10} molekül formülüne sahip olup optikçe aktif değildir ve ayrı ayrı enantiyomerlerine ayrılamaz. **G** bileşiği, C_6H_{10} molekül formülüne sahiptir ve optikçe aktiftir. **G** bileşiği üçlü bağ içermez. Katalitik hidrojenlemeyle **G** bileşiği **H**'yi oluşturmaktadır. **H** bileşiği, C_6H_{14} molekül formülüne sahiptir, optikçe aktiftir ve ayrı ayrı enantiyomerlerine ayrılamaz.

7.43 (a)



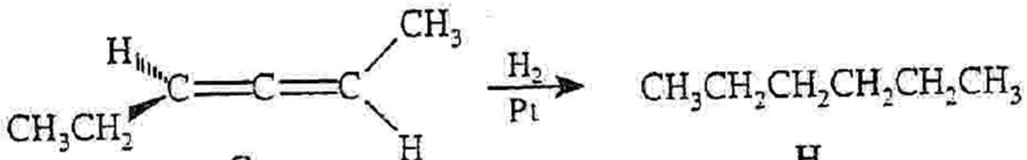
E

F

Optically active (the enantiomeric form is an equally valid answer)

Optically inactive and nonresolvable

(b)



G

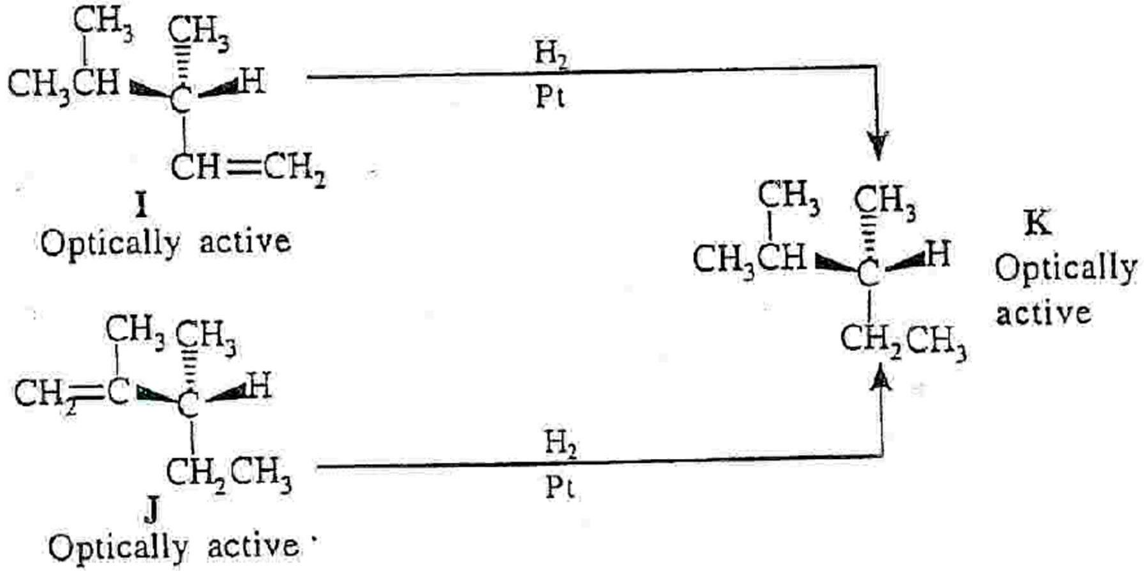
H

Optically active (the enantiomeric form is an equally valid answer)

Optically inactive and nonresolvable

7.44 **I** ve **J** bileşikleri, C_7H_{14} molekül formülüne sahiptir. **I** ve **J** bileşiklerinin her ikisi de optikçe aktiftir ve her ikisi de düzlem polarize ışığı aynı yöne döndürür. Katalitik hidrojenlemeyle **I** ve **J** aynı bileşik olan **K**'yı (C_7H_{16}) oluşturur. **K** bileşiği optikçe aktiftir. **I**, **J** ve **K** bileşikleri için olası yapıları öneriniz.

7.44 That I and J rotate plane-polarized light in the same direction tells us that I and J are not enantiomers of each other. Thus, the following are possible structures for I, J, and K. (The enantiomers of I, J, and K would form another set of structures, and other answers are possible as well.)



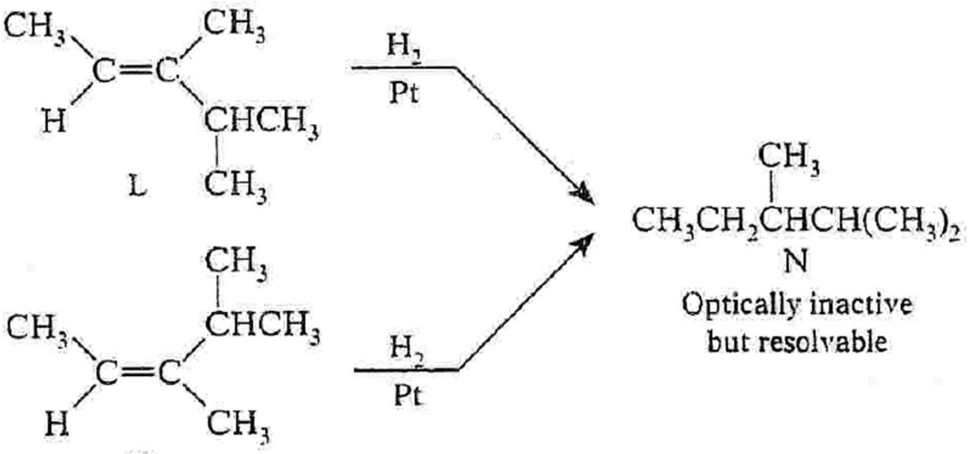
I
Optically active

J
Optically active

K
Optically active

7.45 **L** ve **M** bileşikleri, C_7H_{14} molekül formülüne sahiptir. Optikçe aktif olmayan **L** ve **M** bileşikleri yarılamazlar ve birbirlerinin diastereomerleridir. Hem **L** hem de **M**'nin katalitik hidrojenlenmesi **N** bileşiğini oluşturur. **N** bileşiği optikçe aktif değildir, fakat ayrı ayrı enantiyomerlerine ayrılabilir. **L**, **M** ve **N** için olası yapılar öneriniz.

7.45 The following are possible structures:



L

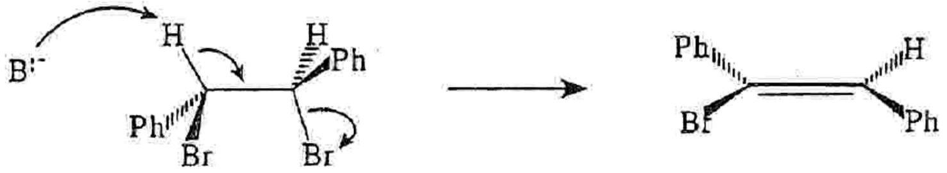
M

N
Optically inactive
but resolvable

(other answers are possible as well)

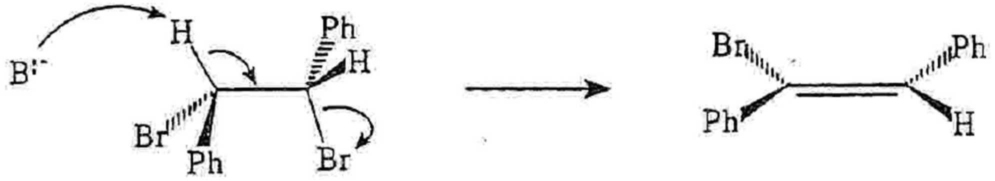
7.46 **(a)** (1*R*, 2*R*)-1,2-Dibromo-1,2-difeniletan veya (1*S*,2*S*)-1,2-dibromo-1,2-difeniletan enantiyomerlerinin (veya ikisinin rasem karışımının) kısmî dehidrahalojenlenmesi (*Z*)-1-bromo-1,2-difenileten verir, oysa (b) (1*R*,2*S*)-1,2difenilmetandan (mezo bileşiği) kısmî hidrojen halojenür çıkarılmasıyla yalnız (*E*)-1-bromo-1,2-difenileten oluşur. **(c)** (1*R*,2*S*)-1,2-dibromo-1,2-difeniletanın aseton içinde sodyum iyodürle etkileştirilmesi yalnızca (*E*) 1,2-difenileten oluşturur. Bu sonuçları açıklayınız.

7.46 (a) With either the (1*R*,2*R*)- or the (1*S*,2*S*)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti periplanar arrangement of the H- and Br-. In either case, the elimination leads only to (*Z*)-1-bromo-1,2-diphenylethene:



(1*R*,2*R*)-1,2-Dibromo-1,2-diphenylethane
(anti periplanar orientation of H- and -Br)

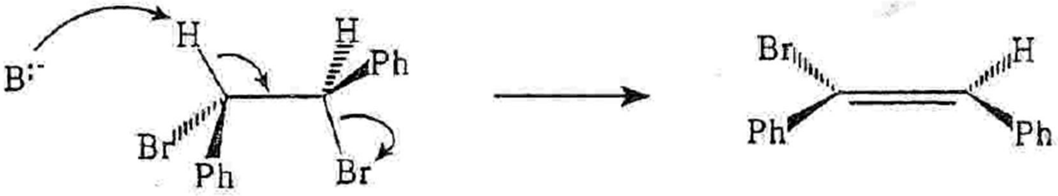
(*Z*)-1-Bromo-1,2-diphenylethene



(1*S*,2*S*)-1,2-Dibromo-1,2-diphenylethane
(anti periplanar orientation of H- and -Br)

(*Z*)-1-Bromo-1,2-diphenylethene

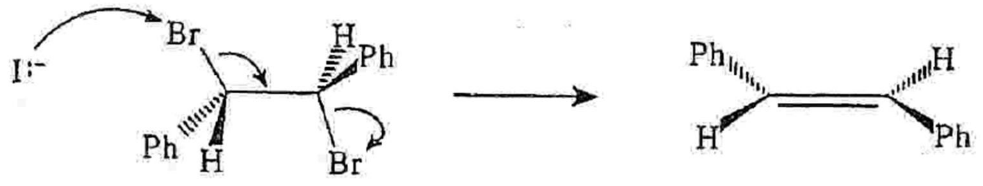
(b) With (1*R*,2*S*)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti periplanar arrangement of the H- and Br-. In this case, the elimination leads only to (*E*)-1-bromo-1,2-diphenylethene:



(1*R*,2*S*)-1,2-Dibromo-1,2-diphenylethane
(anti periplanar orientation of H- and -Br)

(*E*)-1-Bromo-1,2-diphenylethene

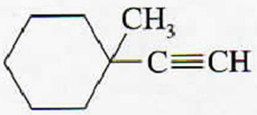
(c) With (1*R*,2*S*)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti periplanar arrangement of both bromine atoms. In this case, the elimination leads only to (*E*)-1,2-diphenylethene:



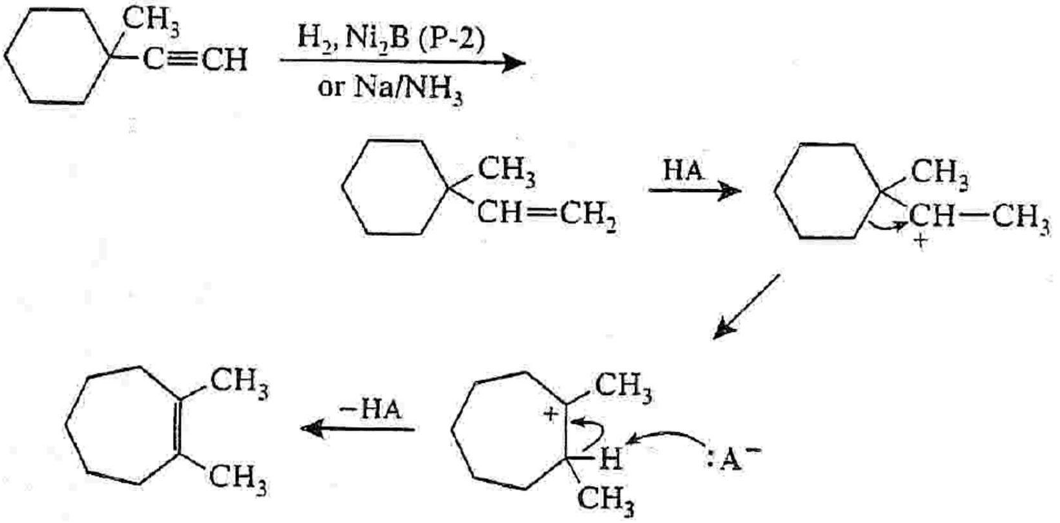
(1*R*,2*S*)-1,2-Dibromo-1,2- diphenylethane
(anti periplanar orientation of both -Br atoms)

(*E*)-1,2- Diphenylethene

*7.47 **(a)** Bu bölümde gördüğümüz tepkimelerden yararlanarak aşağıdaki alkinin, Problem 7.38 (b)'de elde edilen ürünün 7 üyeli bir homoloğu olan bileşiğe nasıl dönüştürülebileceğini gösteriniz. **(b)** Bu iki durumda elde edilen homolog ürünlerin yapıları için 1620–1680cm^{-1} bölgelerinde gözlenen soğurmalarına güvenilebilir mi?



*7.47 (a)



(b) No, tetrasubstituted double bonds usually show no C=C stretching absorption in their infrared spectra.

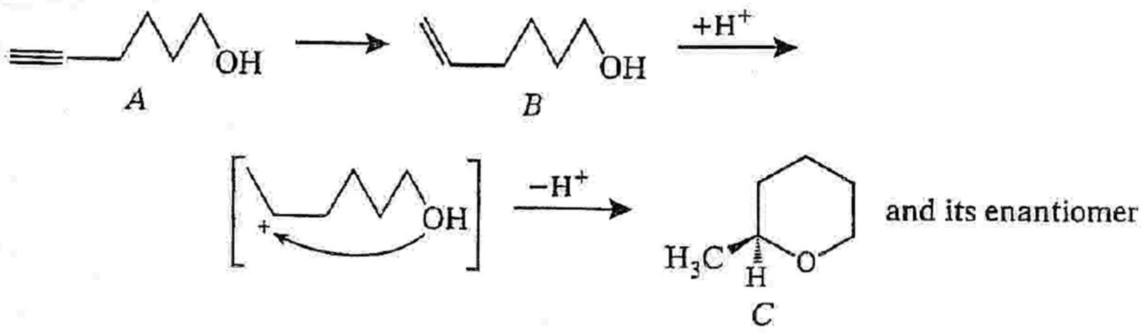
*7.48 **A, B** ve **C** Bileşiklerinin yapılarını tahmin ediniz:

A Bileşiği, dallanmamış bir altı karbonlu alkin (C_6) ve aynı zamanda bir birincil alkoldür.

B bileşiği, **A** bileşiğinden, hidrojen ve nikel borür katalizörü veya çözünen metal indirgemesi yöntemi kullanılarak elde edilir.

C bileşiği, **B** bileşiğinin, oda sıcaklığında sulu asitle etkileştirilmesiyle oluşturulur. **C** bileşiği, 1620–1680 cm^{-1} veya 3590–3650 cm^{-1} bölgelerinde infrared soğurması göstermez. Bu bileşiğin, hidrojen eksikliği indeksi birdir ve bir stereomerkeze sahiptir; fakat rasemat olarak oluşur.

*7.48



***7.49** Aşağıdaki bileşiklerin hidrojen eksikliği indeksleri kaçtır?

(a) $C_7H_{10}O_2$

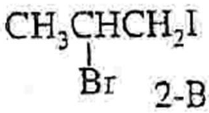
(b) $C_5H_4N_4$

*7.49 (a) Three
(b) Six

Alkenler ve Alkinler II: Katılma Tepkimeleri

Propene, IBr'nin iyonik katılmasından elde edilebilecek ürünün yapısını ve adını yazınız. ◄ **Problem 8.1**

8.1

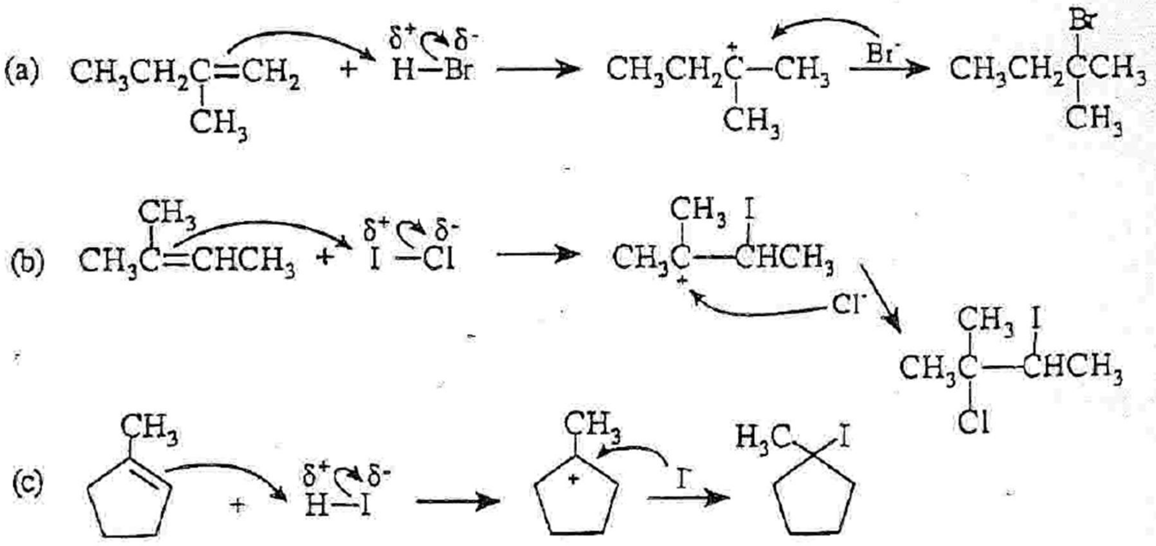


$$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_2I$$

2-Bromo-1-iodopropane

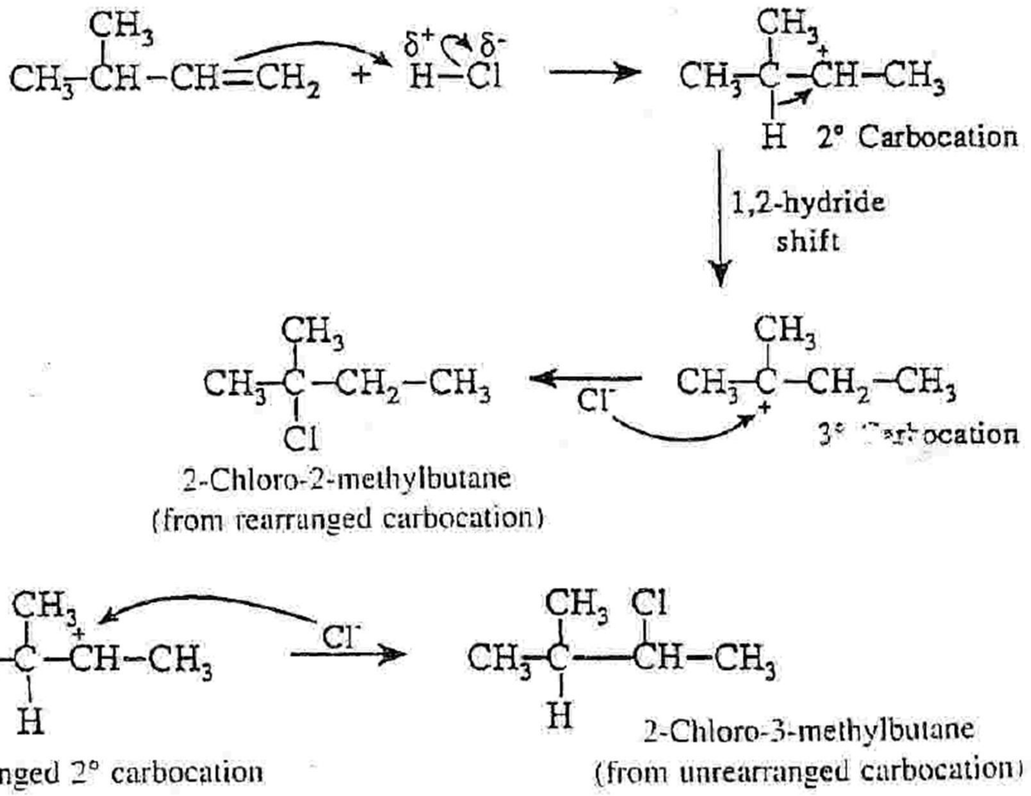
(a) 2-Metil-1-bütene HBr katılmasının, (b) 2-Metil-2-bütene ICl katılmasının ve (c) 1-metilsiklopentene HI katılmasının mekanizmasını tasarlayınız. ◄ **Problem 8.2**

8.2

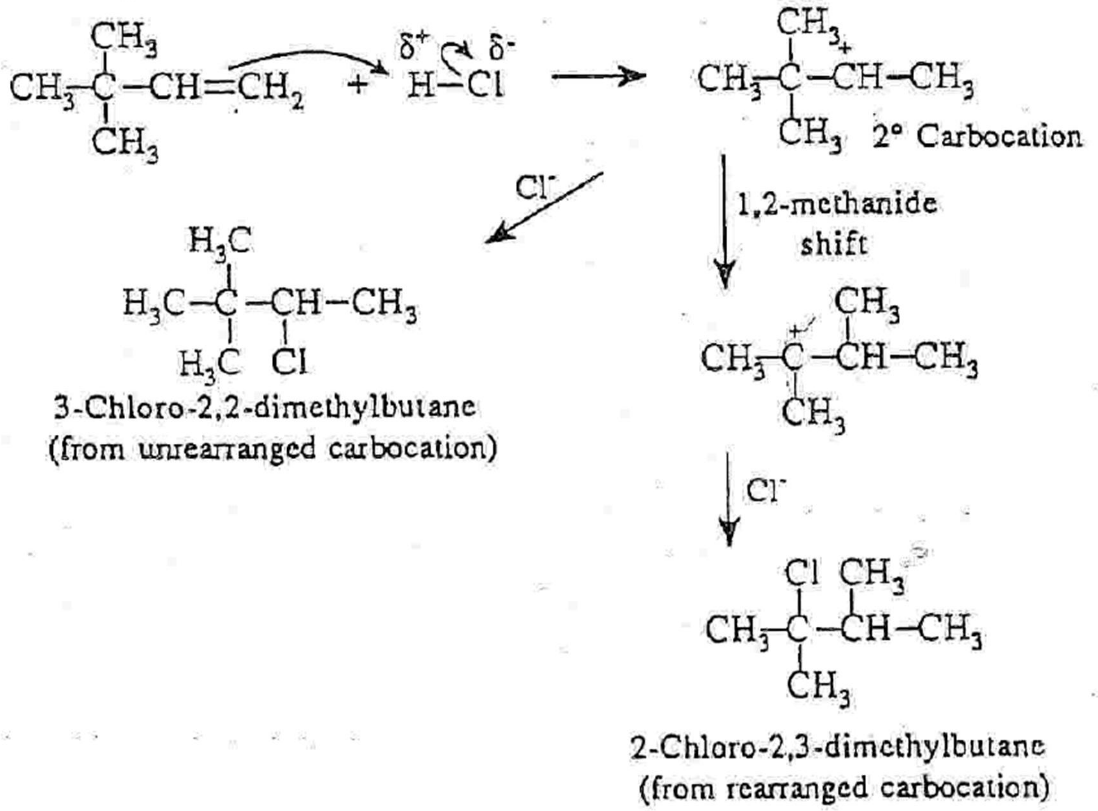


Aşağıdaki tepkimeler için mekanizmalı açıklamalar yapınız: (a) 3-Metil-1-bütene hidrojen klorür katılması iki ürün oluşturur: 2-kloro-3-metilbütan ve 2-kloro-2-metilbütan, (b) 3,3-Dimetil-1-bütene hidrojen klorür katılması iki ürün verir: 3-kloro-2,2-dimetilbütan ve 2-kloro-2,3-dimetilbütan. (Bu tepkimelerin her ikisinin de ilerleyişinin açıklamaları F. Whitmore tarafından yapılmıştır (bkz. Altbölüm 7.7A). ◄ **Problem 8.3**

8.3 (a)



(b)


δ+ δ-
2° Carbocation
Cl⁻
1,2-methanide shift
3-Chloro-2,2-dimethylbutane
(from unrearranged carbocation)
2-Chloro-2,3-dimethylbutane
(from rearranged carbocation)

Problem 8.4

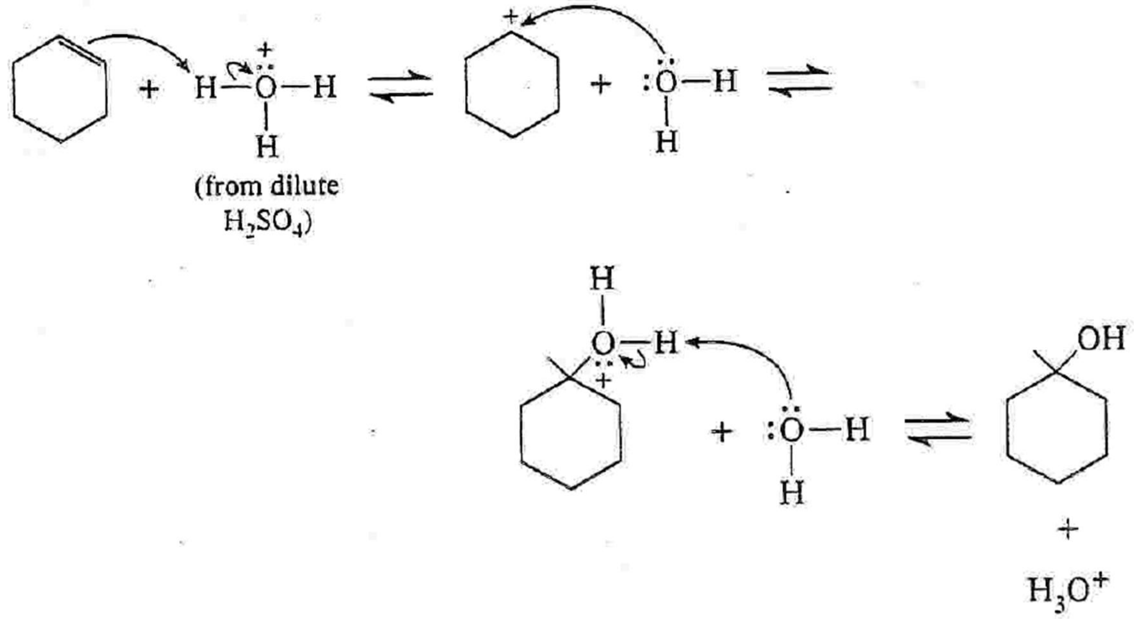
Etanolün bir endüstriyel sentezinde, eten önce %95'lik sülfürik asit içerisinde çözülür. İkinci basamakta su ilave edilir ve karışım ısıtılır. Meydana gelen tepkimeleri açıklayınız.

8.4 $CH_2{=}CH_2 + H_2SO_4 \longrightarrow CH_3CH_2OSO_3H \xrightarrow[\text{heat}]{H_2O} CH_3CH_2OH + H_2SO_4$

Problem 8.5

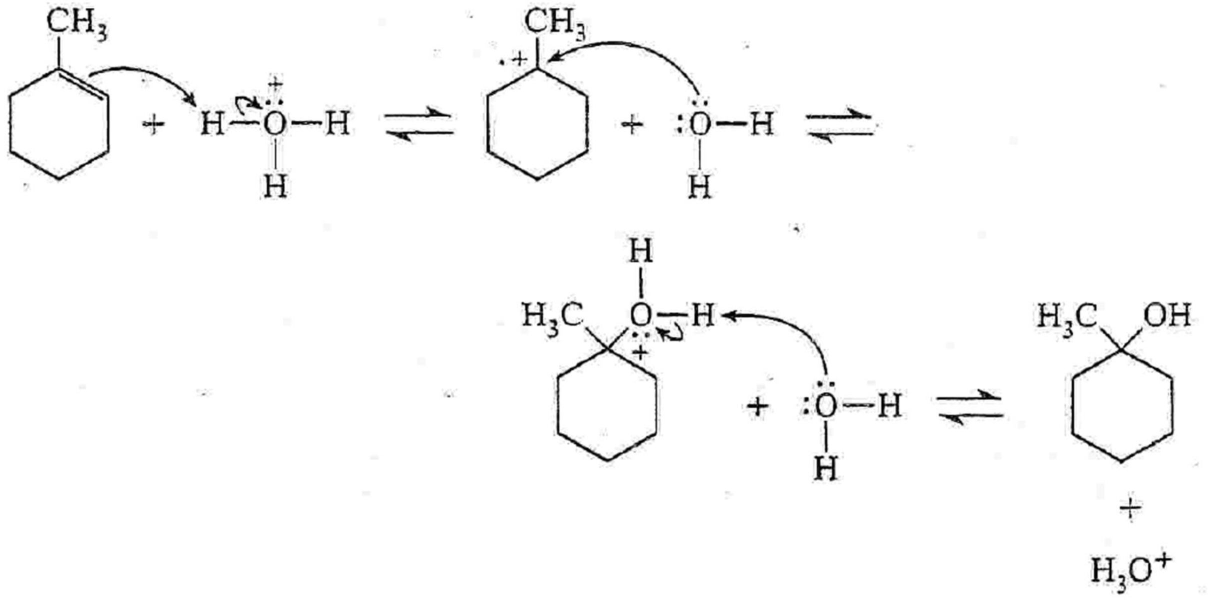
(a) Sikloheksanol elde etmek için yapılan sikloheksenin asit–katalizli hidrasyonundaki bütün basamakları gösteriniz ve iyi bir ürün verimi almak için kullanacağınız genel koşulları belirtiniz. (b) Tersi olan tepkimeyi, sikloheksen eldesi için sikloheksanolün dehidrasyonunu gerçekleştirmek için kullanacağınız genel koşulları belirtiniz. (c) 1-Metilsikloheksene asit–katalizli su katılmasından hangi ürünü elde etmeyi umarsınız? Cevabınızı açıklayınız.

8.5 (a) Use a high concentration of water because we want the carbocation produced to react with water. And use a strong acid whose conjugate base is a very weak nucleophile. (For this reason we would not use HI, HBr, or HCl.) An excellent method, therefore, is to use dilute sulfuric acid.



(b) Use a low concentration of water (i.e., use concentrated H_2SO_4) and use a higher temperature to encourage elimination.

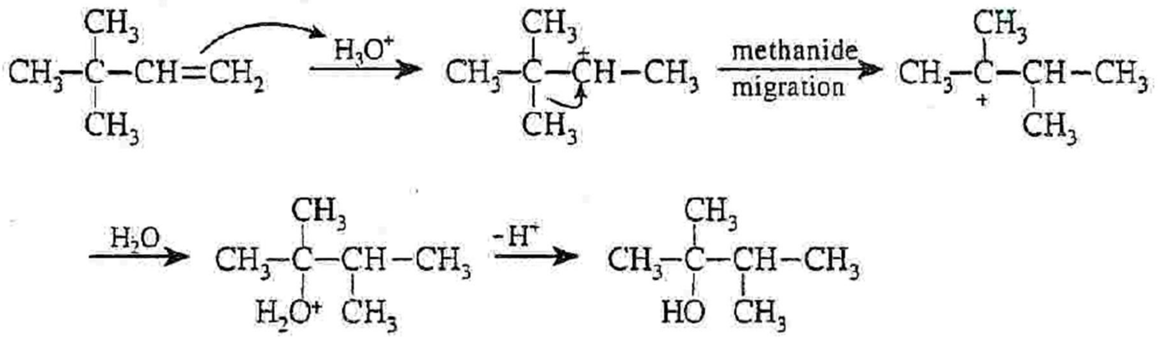
(c) 1-Methylcyclohexanol would be the product because a 3° carbocation would be formed as the intermediate.



Problem 8.6

3,3-Dimetil-1-bütenin asit katalizli hidrasyonunda 2,3-dimetil-2-bütanolün nasıl oluştuğunu gösteren bir mekanizmadaki tüm basamakları açıklayınız.

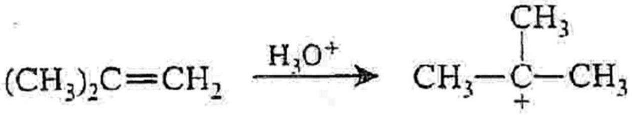
8.6



Aşağıdaki alkenlerin asit katalizli hidrasyonunda aşağıdaki etkinlik sırası gözlenir. ◀ **Problem 8.7**

$$(CH_3)_2C{=}CH_2 > CH_3CH{=}CH_2 > CH_2{=}CH_2$$

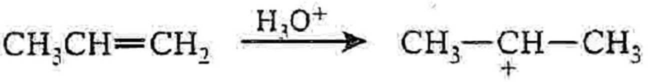
8.7 The order reflects the relative ease with which these alkenes accept a proton and form a carbocation. $(CH_3)_2C{=}CH_2$ reacts faster because it leads to a tertiary cation.



$$(CH_3)_2C{=}CH_2 \xrightarrow{H_3O^+} CH_3-\overset{\displaystyle CH_3}{\underset{+}{C}}-CH_3$$

3° Carbocation

$CH_3CH{=}CH_2$ leads to a secondary cation.



$$CH_3CH{=}CH_2 \xrightarrow{H_3O^+} CH_3-\underset{+}{CH}-CH_3$$

2° Carbocation

and $CH_2{=}CH_2$ reacts most slowly because it leads to a primary carbocation.

$$CH_2{=}CH_2 \xrightarrow{H_3O^+} CH_3-CH_2^{\,+}$$

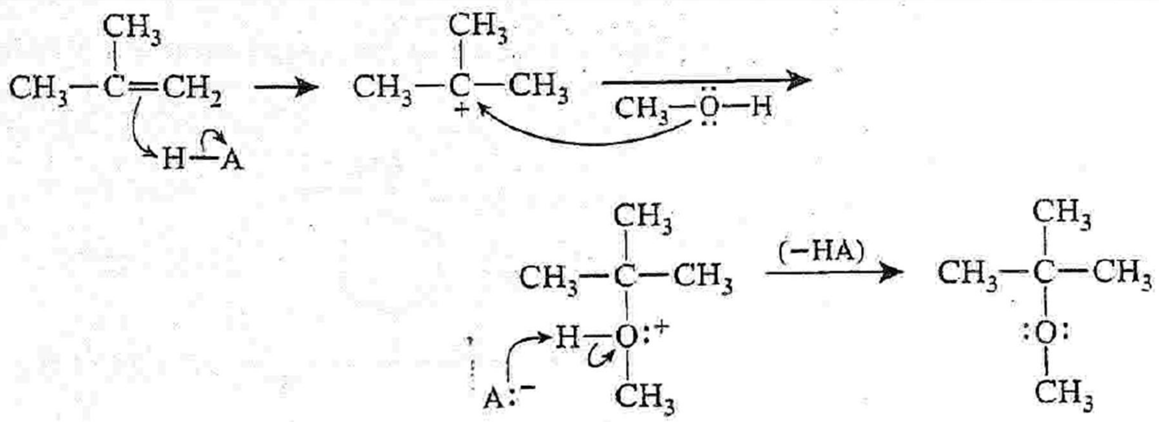
1° Carbocation

Recall that formation of the carbocation is the rate-determining step in acid-catalyzed hydration and that the order of stabilities of carbocations is the following:

$$3° > 2° > 1° > {}^{+}CH_3$$

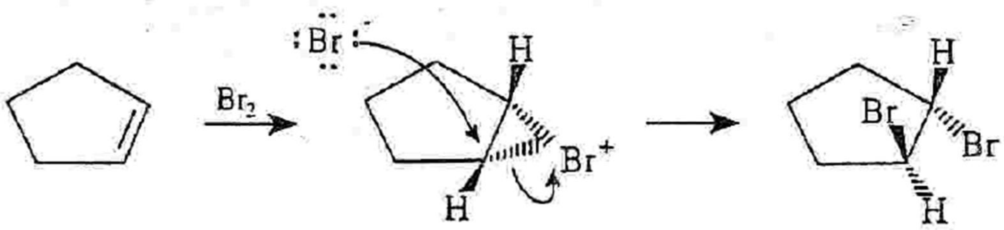
2-Metilpropen (izobütilen), kuvvetli bir asit içeren metanol içerisinde çözündüğünde *ter*-bütil metil eter, $CH_3O(CH_3)_3$, oluşturan bir tepkime meydana gelir. Bunu açıklayan bir mekanizma yazınız. ◀ **Problem 8.8**

8.8

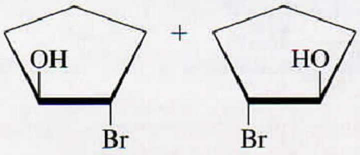


Altbölüm 8.7'de, siklopentene brom katıldığında *trans*-1,2-dibromosiklopentanın bir enantiyomerinin oluşumuna ait bir mekanizmayı öğrendiniz. Şimdi, diğer enantiyomerin nasıl oluştuğunu gösteren bir mekanizma yazınız. ◀ **Problem 8.9**

8.9

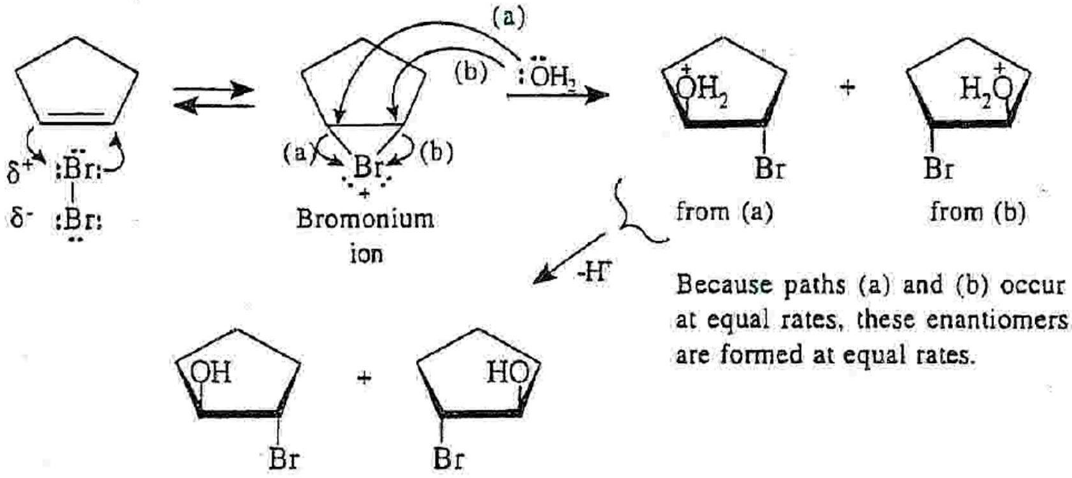


Problem 8.10 ➤ Siklopenten bromun bir sulu çözeltisiyle etkileştirildiğinde *trans*-2-bromosiklopentanol ve enantiyomeri oluşur. Bunu açıklayan bir mekanizma öneriniz.



***trans*-2-Bromosiklopentanol enantiyomerleri**

8.10

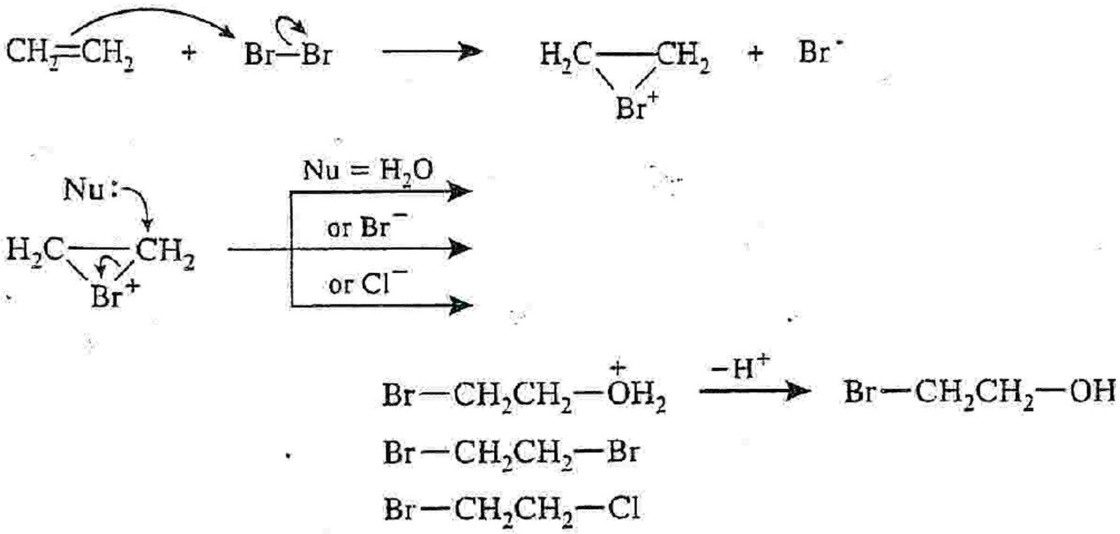


Because paths (a) and (b) occur at equal rates, these enantiomers are formed at equal rates.

Racemic form

Problem 8.11 ➤ Eten gazı, brom ve sodyum klorürün bir sulu çözeltisinden geçirildiğinde tepkimenin ürünleri $BrCH_2CH_2Br$, $BrCH_2CH_2OH$ ve $BrCH_2CH_2Cl$'dir. Her bir ürünün nasıl oluştuğunu mekanizmalarıyla yazarak gösteriniz.

8.11



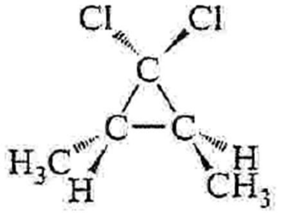
Problem 8.12 ➤ Aşağıdaki tepkimelerin her birinden hangi ürünün oluşacağını umuyorsunuz?

(**a**) *trans*-2-Büten $\xrightarrow[\text{CHCl}_3]{\text{KOC(CH}_3)_3}$

(**b**) Siklopenten $\xrightarrow[\text{CHBr}_3]{\text{KOC(CH}_3)_3}$

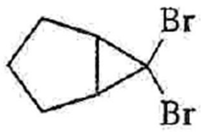
(**c**) *cis*-2-Büten $\xrightarrow[\text{dietil eter}]{\text{CH}_2\text{I}_2\text{/Zn(Cu)}}$

8.12 (a)

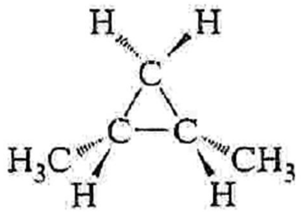


+ enantiomer

(b)

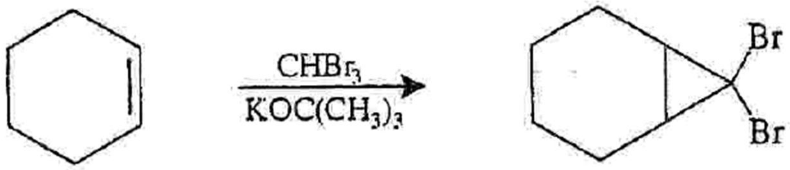


(c)



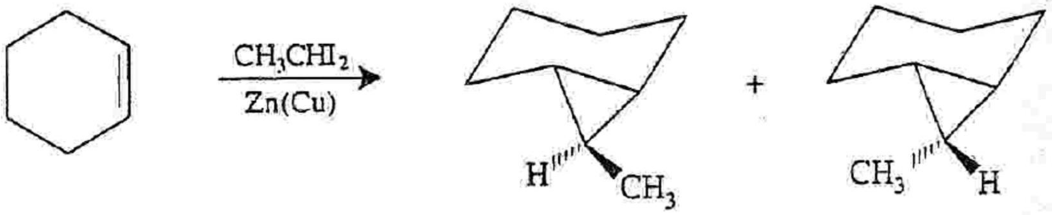
Problem 8.13 ➤ Sikloheksenden başlayarak ve herhangi diğer ihtiyaç duyulan reaktifleri kullanarak, 7,7-dibromobisiklo[4,1,0]heptanın sentezini tasarlayınız.

8.13



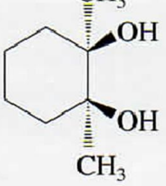
Problem 8.14 ➤ Sikloheksenin 1,1-diiyodoetan ve bir çinko–bakır ikilisiyle etkileştirilmesi iki izomerik ürünün oluşmasına yol açar. Bunların yapıları nasıldır?

8.14

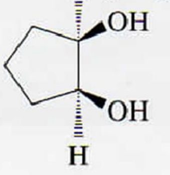


Problem 8.15 ➤ Bir alkenden başlayarak aşağıdakilerden her birinin sentezini tasarlayınız:

(**a**)

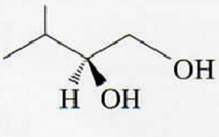


(**b**)



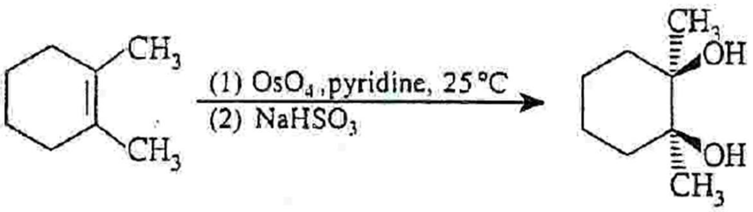
(ve enantiyomeri)

(**c**)

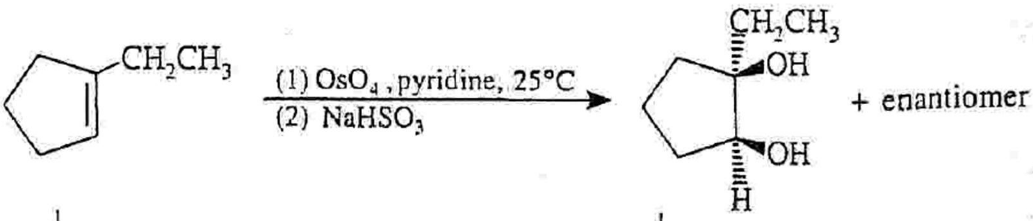


(ve enantiyomeri)

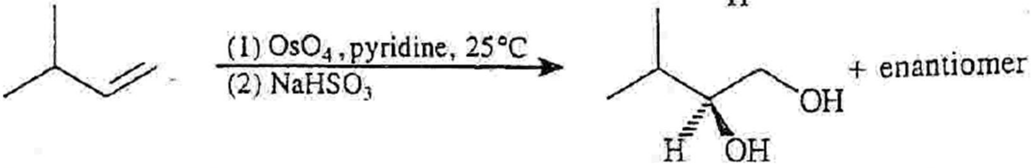
8.15 (a)



(b)

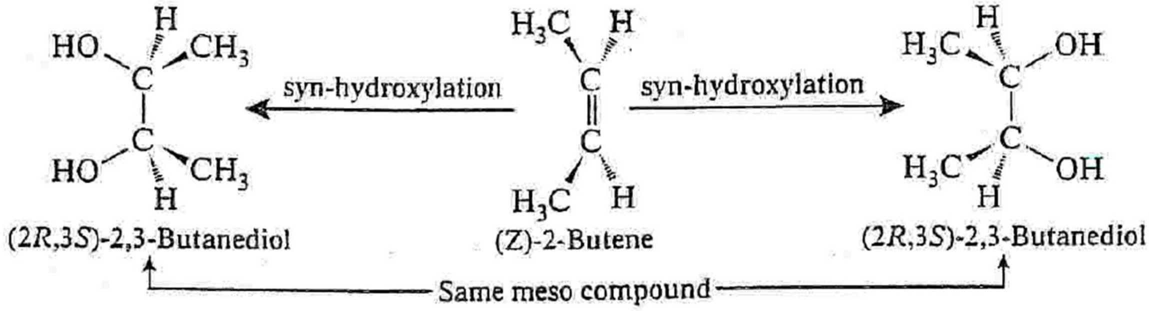


(c)

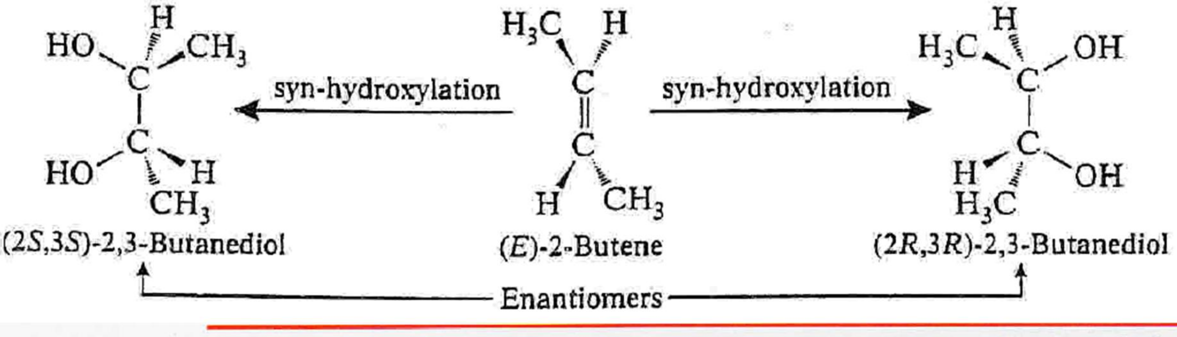


Problem 8.16 ➤ Aşağıdaki olayları açıklayınız: (a) (*Z*)-2-Bütenin piridin içerisindeki OsO$_4$ ve sonra NaHSO$_3$ ile etkileştirilmesi optikçe aktif olmayan ve enantiyomerlerine yarılamayan bir diol verir. (b) (*E*)-2-Bütenin OsO$_4$ ve sonra NaHSO$_3$ ile etkileştirilmesi optikçe aktif olmayan fakat enantiyomerlerine yarılabilen bir diol verir.

8.16 (a) Syn-hydroxylation at either face of (*Z*)- or cis-alkene leads to the meso compound (2*R*,3*S*)-2,3-butanediol.



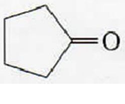
(b) Syn-hydroxylation at one face of the (*E*)- or trans-alkene leads to the (2*R*,3*R*)-enantiomer; at the other face, which is equally likely, it leads to the (2*S*,3*S*)-enantiomer.



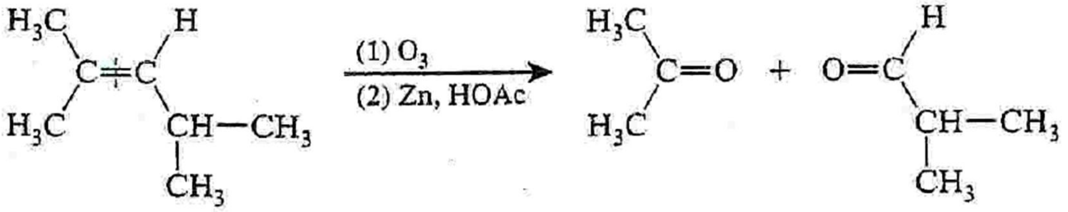
Problem 8.17 ➤ Ozon ve daha sonra çinko ve asetik asitle etkileştirildiğinde aşağıdaki ürünleri verebilecek olan alkenlerin yapılarını yazınız.

(a) CH_3COCH_3 ve $CH_3CH(CH_3)CHO$

(b) Yalnız CH_3CH_2CHO (bir mol alkenden 2 mol oluşur)

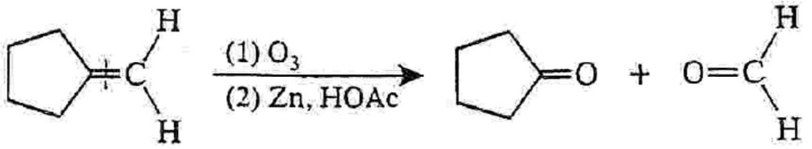
(c)  ve HCHO

8.17 (a)



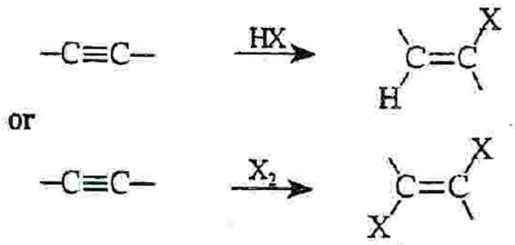
(b) $CH_3CH_2CH{=}CHCH_2CH_3 \xrightarrow[(2)\ Zn,\ HOAc]{(1)\ O_3} CH_3CH_2CH{=}O$

(c)



Alkenler, elektrofilik reaktiflerin (Br_2, Cl_2 veya HCl gibi) katılmalarına karşı alkinlerden daha etkindirler. Alkinler ile bu elektrofilik reaktiflerin aynılarının bir eşdeğer molü etkileştirildiğinde katılmayı "alken basamağında" durdurmak kolaydır. Bu durum mantıksız gibi görünmektedir, fakat öyle değildir. Bunu açıklayınız. ◄ **Problem 8.18**

8.18 Ordinary alkenes *are* more reactive toward electrophilic reagents. But the alkenes obtained from the addition of an electrophilic reagent to an alkyne have at least one electronegative atom (Cl, Br, etc.) attached to a carbon atom of the double bond.



These alkenes are less reactive than alkynes toward electrophilic addition because the electronegative group makes the double bond "electron poor."

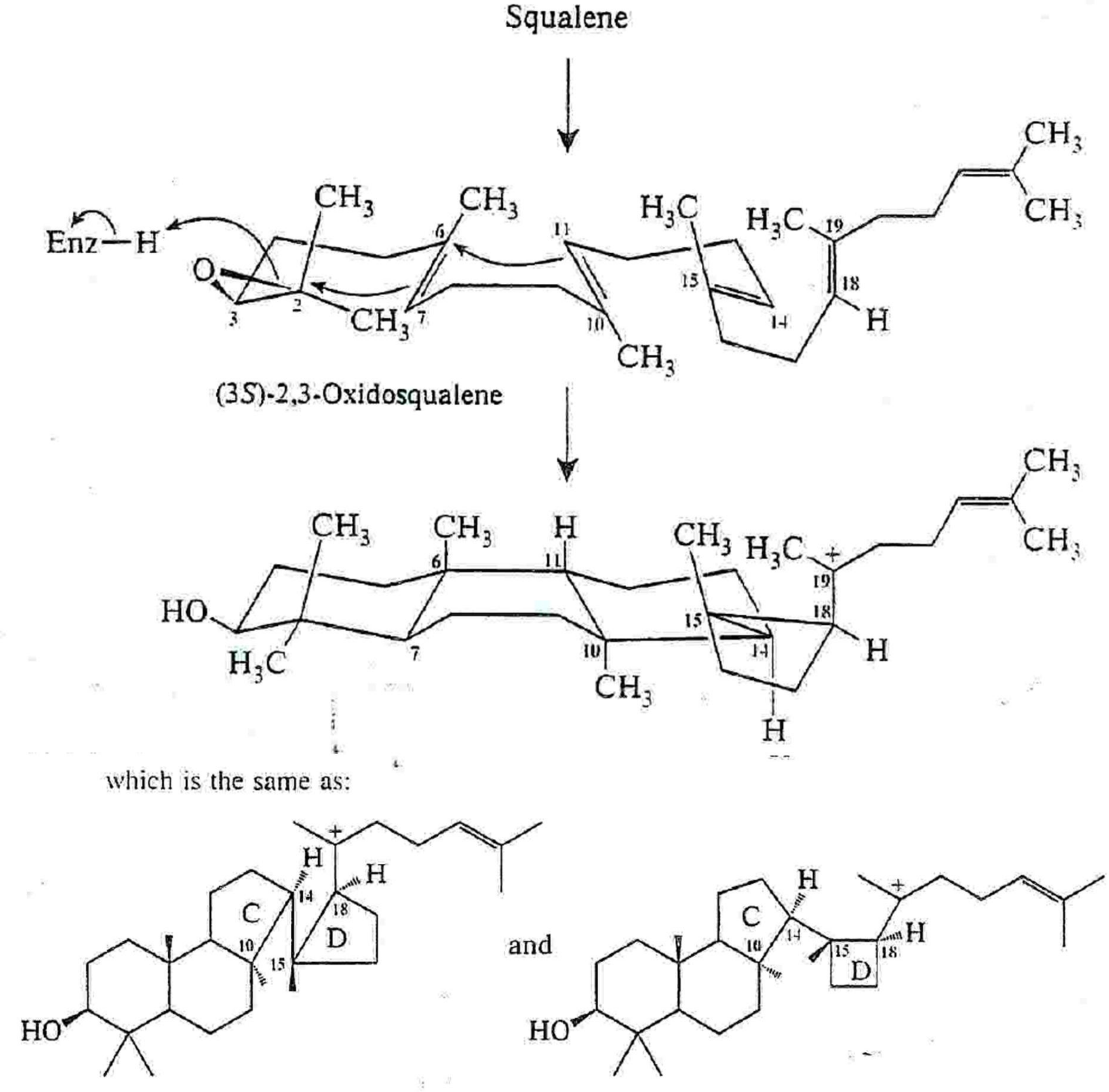
Problem 8.19 ➤ **A** ve **B** alkinleri, C_8H_{14} molekül formülüne sahiptir. Bileşik **A** veya **B**, bir metal katalizör varlığında aşırı hidrojenle etkileştirilirse oktan oluşur. Bir **C** bileşiğinin (C_8H_{12}) de benzer şekilde etkileştirilmesi C_8H_{16} formülüne sahip bir ürün verir. Alkin **A**'nın önce ozon ve daha sonra asetik asitle etkileştirilmesi tek bir ürün, $CH_3CH_2CH_2CO_2H$ oluşturur. Alkin **C**'nin de önce ozon ve daha sonra suyla etkileştirilmesi yine tek bir ürün, $HO_2C(CH_2)_6CO_2H$ verir. **B** bileşiğinin İR spekturumunda ~3300cm^{-1}'de bir soğurması vardır. **A**, **B** ve **C** bileşikleri nelerdir?

8.19 The molecular formula and the formation of octane from A and B indicate that both compounds are unbranched octynes. Since A yields only $CH_3CH_2CH_2CO_2H$ on ozonolysis, A must be the symmetrical octyne $CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3$. The IR absorption for **B** shows the presence of a terminal triple bond. Hence B is $CH_3(CH_2)_5C{\equiv}CH$.

Since C (C_8H_{12}) gives $HO_2C(CH_2)_6CO_2H$ on ozonolysis, C must be cyclooctyne. This is supported by the molecular formula of C and the fact that it is converted to C_8H_{16} (cyclooctane) on catalytic hydrogenation.

Answer to the Study Problem related to cholesterol biosynthesis, page 355.

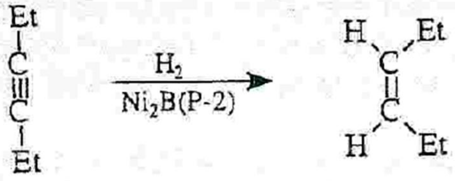
In cholesterol biosynthesis an anti-Markovnikov addition occurs between C10 (once it becomes like a tertiary carbocation) and C15, forming the six-membered "C" ring of cholesterol (see the reactions in the text, page 355). This process results in a developing *secondary* carbocation at C14, which adds to C18 to form the five-membered "D" ring of cholesterol. If, on the other hand, Markovnikov addition occurred between C10 and C14 instead of anti-Markovnikov addition between C10 and C15, as shown in the following scheme, a developing *tertiary* carbocation would result at C15, along with formation of a five-membered "C" ring. Then, Markovnikov addition of C15 (as it becomes like a tertiary carbocation) to C18 would lead to a four-membered "D" ring and a tertiary carbocation at C19.



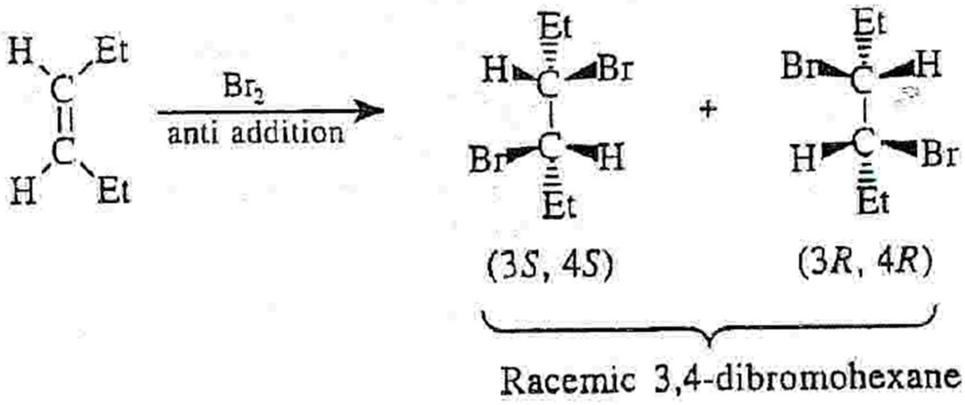
Problem 8.20

(3*R*,4*R*)- ve (3*S*,4*S*)-Dibromoheksenin bir rasemik şeklini sentezlemek için örnek problemde verilen işlemleri nasıl değiştirirdiniz?

8.20 By converting the 3-hexyne to *cis*-3-hexene using H_2/Ni_2B (P-2).



Then, addition of bromine to *cis*-3-hexene will yield (3*R*,4*R*), and (3*S*,4*S*)-3,4-dibromohexane as a racemic form.



8.21 1-Büten aşağıdaki reaktiflerin her biriyle tepkimeye girdiğinde oluşan ürünün yapı formüllerini yazınız:

(a) HI

(b) H_2, Pt

(c) Sey. H_2SO_4, ılık

(d) Soğuk derişik H_2SO_4

(e) Soğuk derişik H_2SO_4, sonra H_2O ve ısı

(f) Alümina varlığında HBr

(g) CCl_4 içerisinde Br_2

(h) CCl_4 içerisinde Br_2, sonra aseton içerisinde KI

(i) H_2O içerisinde Br_2

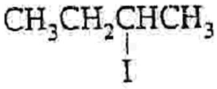
(j) Alümina varlığında HCl

(k) Soğuk derişik $KMnO_4$, OH^-

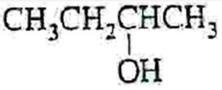
(l) O_3, sonra Zn, HOAc

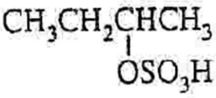
(m) OsO_4, sonra $NaHSO_3/H_2O$

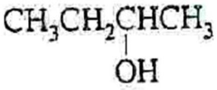
(n) $KMnO_4$, OH^-, ısı, sonra H_3O^+

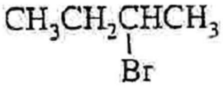
8.21 (a)

$CH_3CH_2\underset{\displaystyle I}{CH}CH_3$

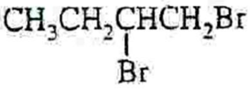
(b) $CH_3CH_2CH_2CH_3$

(c)

$CH_3CH_2\underset{\displaystyle OH}{CH}CH_3$

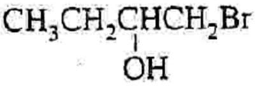
(d)

$CH_3CH_2\underset{\displaystyle OSO_3H}{CH}CH_3$

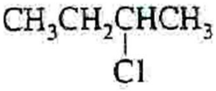
(e)

$CH_3CH_2\underset{\displaystyle OH}{CH}CH_3$

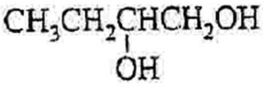
(f)

$CH_3CH_2\underset{\displaystyle Br}{CH}CH_3$

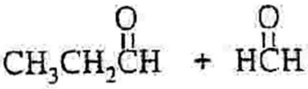
(g)

$CH_3CH_2\underset{\displaystyle Br}{CH}CH_2Br$

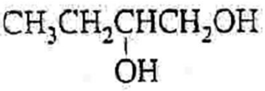
(h) $CH_3CH_2CH{=}CH_2$

(i)

$CH_3CH_2\underset{\displaystyle OH}{CH}CH_2Br$

(j)

$CH_3CH_2\underset{\displaystyle Cl}{CH}CH_3$

(k)

$CH_3CH_2\underset{\displaystyle OH}{CH}CH_2OH$

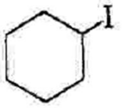
(l)

$CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}H + H\overset{\displaystyle O}{\overset{\|}{C}}H$

(m)

$CH_3CH_2\underset{\displaystyle OH}{CH}CH_2OH$

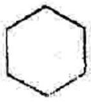
(n) $CH_3CH_2CO_2H + CO_2$

8.22 1-Büten yerine siklohekseni kullanarak problem 8.21'i tekrarlayınız.

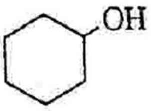
8.22 (a)



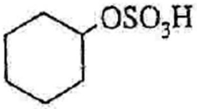
(b)



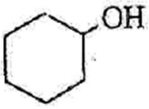
(c)



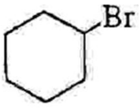
(d)



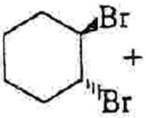
(e)



(f)

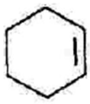


(g)

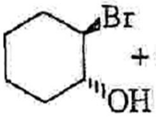


+ enantiomer

(h)

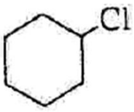


(i)

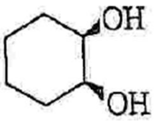


+ enantiomer

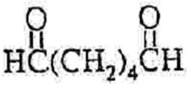
(j)



(k)

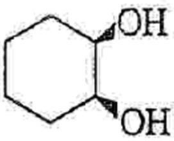


(l)

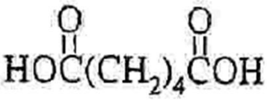


$H\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}H$

(m)



(n)



$HO\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OH$

8.23 1-Bütinin aşağıdakilerin her biriyle olan tepkimesinden oluşmasını beklediğiniz ürünlerin yapısını yazınız.

(a) Bir eşdeğer mol Br_2

(b) Alümina varlığında bir eşdeğer mol HBr

(c) Alümina varlığında iki eşdeğer mol HBr

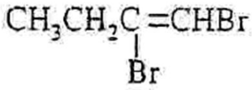
(d) H_2 (aşırı)/Pt

(e) H_2, Ni_2B (P-2)

(f) Sıvı NH_3 içerisinde $NaNH_2$, sonra CH_3I

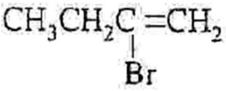
(g) Sıvı NH_3 içerisinde $NaNH_2$, sonra $(CH_3)_3CBr$

8.23 (a)



$CH_3CH_2\underset{\underset{Br}{|}}{C}=CHBr$

(b)



$CH_3CH_2\underset{\underset{Br}{|}}{C}=CH_2$

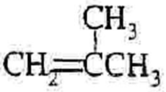
(c) $CH_3CH_2CBr_2CH_3$

(d) $CH_3CH_2CH_2CH_3$

(e) $CH_3CH_2CH=CH_2$

(f) $CH_3CH_2C\equiv CCH_3$

(g) $CH_3CH_2C\equiv CH$ and

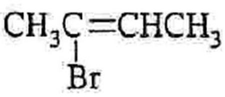


$CH_2=\overset{\overset{CH_3}{|}}{C}CH_3$

[An E2 reaction would take place when $CH_3CH_2C\equiv CNa$ is treated with $(CH_3)_3CBr$.]

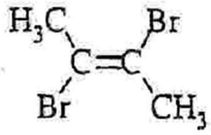
8.24 2-Bütinin aşağıdakilerden her biriyle olan tepkimesinden (eğer tepkime verirse) oluşmasını beklediğiniz ürünlerin yapısını yazınız.

(a) Alümina varlığında bir eşdeğer mol HBr
(b) Alümina varlığında iki eşdeğer mol HBr
(c) Bir eşdeğer mol Br_2
(d) İki eşdeğer mol Br_2
(e) H_2, Ni_2B(P-2)
(f) Alümina varlığında bir eşdeğer mol HCl
(g) Li/sıvı NH_3
(h) H_2 (aşırı)/Pt
(i) İki eşdeğer mol H_2, Pt
(j) $KMnO_4$, OH, sonra H_3O^+
(k) O_3, HOAc
(l) $NaNH_2$, sıvı NH_3

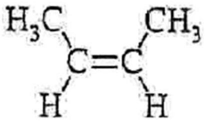
8.24 (a) 

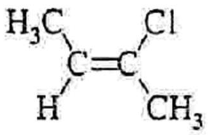
$CH_3\underset{\displaystyle Br}{\underset{|}{C}}{=}CHCH_3$

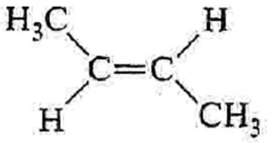
(b) $CH_3CBr_2CH_2CH_3$

(c) 

(d) $CH_3CBr_2CBr_2CH_3$

(e) 

(f) 

(g) 

(h) $CH_3CH_2CH_2CH_3$

(i) $CH_3CH_2CH_2CH_3$

(j) CH_3CO_2H (2 molar equivalents)

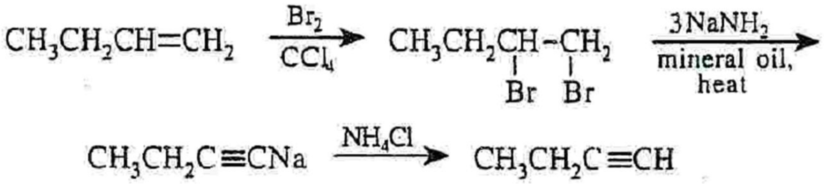
(k) CH_3CO_2H (2 molar equivalents)

(l) no reaction

8.25 1-Bütinin, aşağıdakilerin her birinden nasıl sentezlenebileceğini gösteriniz.

(a) 1-Büten
(b) 1-Klorobütan
(c) 1-Kloro-1-büten
(d) 1,1-Diklorobütan
(e) Etin ve etil bromür

8.25 (a)



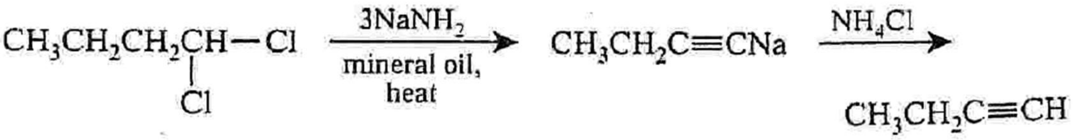
$$\mathrm{CH_3CH_2CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} CH_3CH_2\underset{Br}{CH}{-}\underset{Br}{CH_2} \xrightarrow[\text{mineral oil, heat}]{3NaNH_2}}$$

$$\mathrm{CH_3CH_2C{\equiv}CNa \xrightarrow{NH_4Cl} CH_3CH_2C{\equiv}CH}$$

(b) $\mathrm{CH_3CH_2CH_2CH_2Cl \xrightarrow[\textit{t}\text{-BuOH, heat}]{\textit{t}\text{-BuOK}} CH_3CH_2CH{=}CH_2}$ Then as in (a)

(c) $\mathrm{CH_3CH_2CH{=}CHCl \xrightarrow[\text{mineral oil, heat}]{2NaNH_2} CH_3CH_2C{\equiv}CNa \xrightarrow{NH_4Cl} CH_3CH_2C{\equiv}CH}$

(d)



$$\mathrm{CH_3CH_2CH_2\underset{Cl}{CH}{-}Cl \xrightarrow[\text{mineral oil, heat}]{3NaNH_2} CH_3CH_2C{\equiv}CNa \xrightarrow{NH_4Cl} CH_3CH_2C{\equiv}CH}$$

(e) $\mathrm{H{-}C{\equiv}C{-}H \xrightarrow[liq.NH_3]{NaNH_2} H{-}C{\equiv}CNa \xrightarrow{CH_3CH_2\text{-}Br} CH_3CH_2C{\equiv}CH}$

8.26 2-Metilpropenden (izobütilen) başlayarak ve diğer gerekli reaktifleri kullanarak aşağıdakilerin her biri için bir sentez tasarlayınız.

(a) $\mathrm{(CH_3)_3COH}$

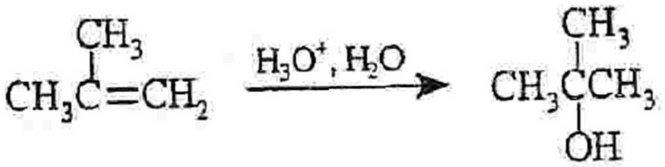
(b) $\mathrm{(CH_3)_3CCl}$

(c) $\mathrm{(CH_3)CBr}$

(d) $\mathrm{(CH_3)_3CF}$

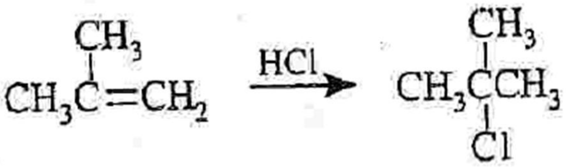
(e) $\mathrm{(CH_3)_2C(OH)CH_2Cl}$

8.26 (a)



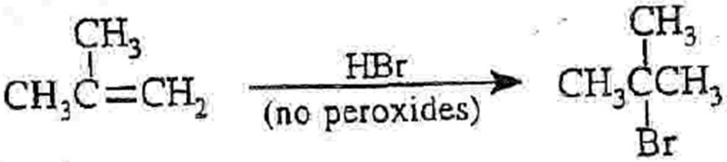
$$\mathrm{CH_3\overset{CH_3}{C}{=}CH_2 \xrightarrow{H_3O^+,\ H_2O} CH_3\overset{CH_3}{\underset{OH}{C}}CH_3}$$

(b)



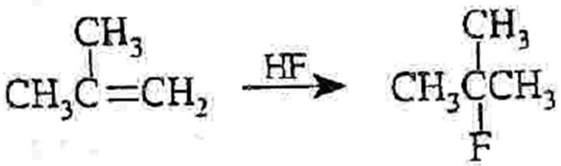
$$\mathrm{CH_3\overset{CH_3}{C}{=}CH_2 \xrightarrow{HCl} CH_3\overset{CH_3}{\underset{Cl}{C}}CH_3}$$

(c)



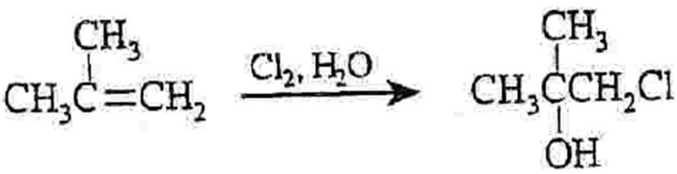
$$\mathrm{CH_3\overset{CH_3}{C}{=}CH_2 \xrightarrow[\text{(no peroxides)}]{HBr} CH_3\overset{CH_3}{\underset{Br}{C}}CH_3}$$

(d)



$$\mathrm{CH_3\overset{CH_3}{C}{=}CH_2 \xrightarrow{HF} CH_3\overset{CH_3}{\underset{F}{C}}CH_3}$$

(e)



$$\mathrm{CH_3\overset{CH_3}{C}{=}CH_2 \xrightarrow{Cl_2,\ H_2O} CH_3\overset{CH_3}{\underset{OH}{C}}CH_2Cl}$$

8.27 Mum ağacının mumunda bulunan güzel kokulu bir bileşik olan mirsen $C_{10}H_{16}$ kapalı formülüne sahiptir ve hiç üçlü bağ içermediği bilinmektedir. **(a)** Mirsenin hidrojen eksikliği indeksi nedir? Mirsen, aşırı hidrojen ve bir platin katalizörle etkileştiğinde formülü $C_{10}H_{22}$ olan bir **A** bileşiğine dönüşmektedir. **(b)** Mirsen kaç halka içermektedir? **(c)** Kaç tane ikili bağ vardır? **A** bileşiğinin 2,6-dimetiloktan olduğu belirlenmiştir. Mirsenin ozonlanması ve ardından çinko ve asetik asitle etkileştirilmesiyle iki mol formaldehit (HCHO), bir mol aseton (CH_3COCH_3) ve formülü $C_5H_6O_3$ olan üçüncü bir **B** bileşiği oluşur. **(d)** Mirsenin yapı formülü nedir? **(e)** **B** bileşiğinin yapı formülü nedir?

8.27 (a) $C_{10}H_{22}$ (saturated alkane)

$\underline{C_{10}H_{16}}$ (formula of myrcene)

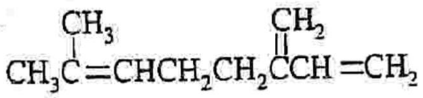
H_6 = 3 pairs of hydrogen atoms

Index of hydrogen deficiency (IHD) = 3

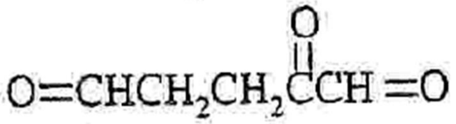
(b) Myrcene contains no rings because complete hydrogenation gives $C_{10}H_{22}$, which corresponds to an alkane.

(c) That myrcene absorbs three molar equivalents of H_2 on hydrogenation indicates that it contains three double bonds.

(d) Three structures are possible; however, only one gives 2,6-dimethyloctane on complete hydrogenation. Myrcene is therefore

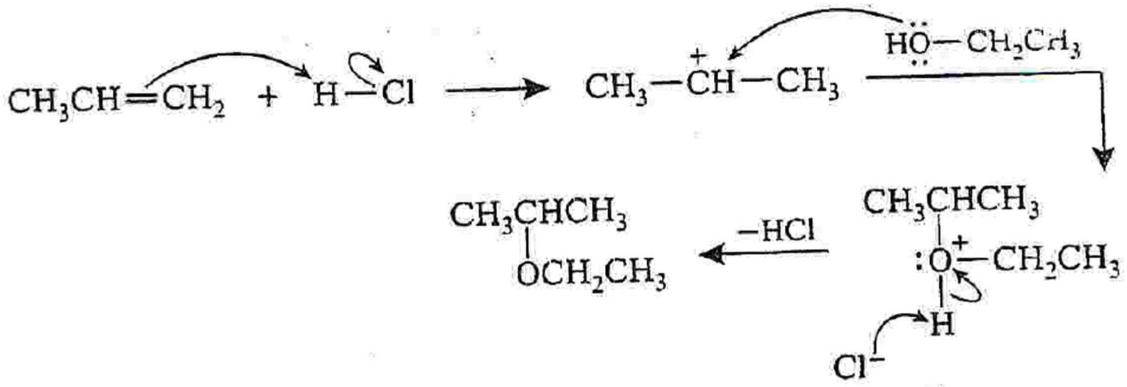


$$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_2CH_2\overset{CH_2}{\overset{\|}{C}}CH=CH_2$$

(e) 

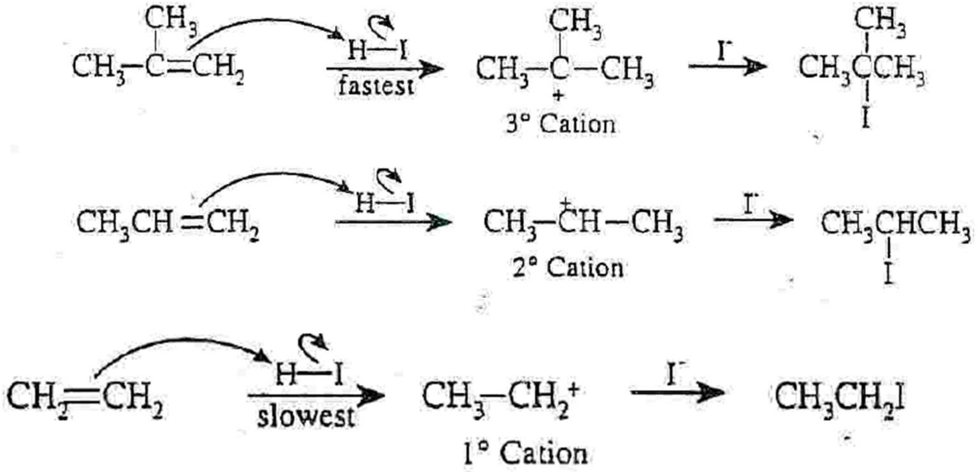
$$O=CHCH_2CH_2\overset{O}{\overset{\|}{C}}CH=O$$

8.28 Propen, etanol içerisinde hidrojen klorürle etkileştirildiğinde tepkimenin ürünlerinden biri etil izopropil eterdir. Bu bileşiğin oluşumuna ilişkin, kabul edilebilir bir mekanizma yazınız.

8.28 

8.29 2-Metilpropen, propen ve eten birbirinden ayrı tepkimelerle aynı koşullar altında, yani aynı derişim ve sıcaklıkta HI ile tepkimeye sokulduğunda, 2-metilpropenin en hızlı ve eterin ise en yavaş etkileştiği saptanmıştır. Bu bağıl hızlar için bir açıklama yapınız.

8.29 The rate-determining step in each reaction is the formation of a carbocation when the alkene accepts a proton from HI. When 2-methylpropene reacts, it forms a 3° carbocation (the most stable); therefore, it reacts fastest. When ethene reacts, it forms a 1° carbocation (the least stable); therefore, it reacts the slowest.



$$CH_3\overset{CH_3}{\overset{|}{C}}{=}CH_2 \xrightarrow[\text{fastest}]{H{-}I} CH_3{-}\underset{+}{\overset{CH_3}{\overset{|}{C}}}{-}CH_3 \xrightarrow{I^-} CH_3\underset{\underset{I}{|}}{\overset{CH_3}{\overset{|}{C}}}CH_3$$

3° Cation

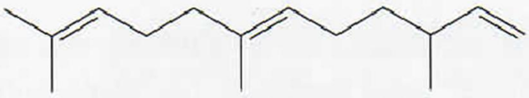
$$CH_3CH{=}CH_2 \xrightarrow{H{-}I} CH_3{-}\overset{+}{C}H{-}CH_3 \xrightarrow{I^-} CH_3\underset{\underset{I}{|}}{C}HCH_3$$

2° Cation

$$CH_2{=}CH_2 \xrightarrow[\text{slowest}]{H{-}I} CH_3{-}CH_2^+ \xrightarrow{I^-} CH_3CH_2I$$

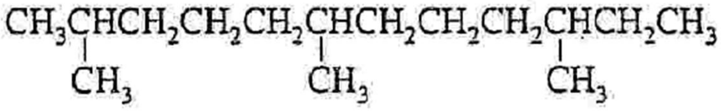
1° Cation

8.30 Farnesen (aşağıda) elmaların kabuğundaki muma benzeyen örtü maddesinde bulunan bir maddedir. Farnesen, bir platin katalizör varlığında aşırı hidrojenle tepkimeye sokulduğunda oluşan bileşiğin yapısını ve IUPAC adını belirtiniz.



Farnesen

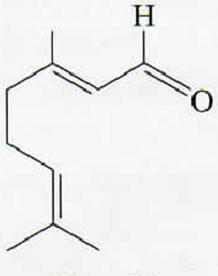
8.30



$$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$$

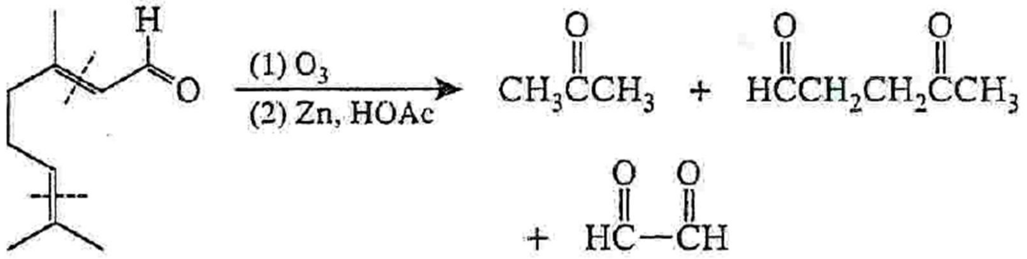
2,6,10-Trimethyldodecane

8.31 Limonotu yağının bir bileşeni olan geranial önce ozon, sonra çinko ve suyla etkileştirildiğinde oluşan bileşiklerin yapı formüllerini yazınız.



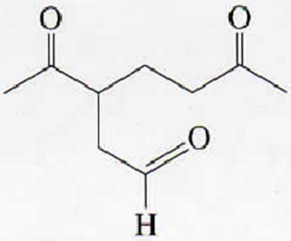
Geranial

8.31

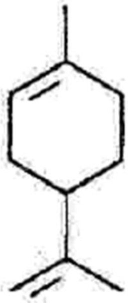


$$\xrightarrow[\text{(2) Zn, HOAc}]{\text{(1) }O_3} CH_3\overset{O}{\overset{\|}{C}}CH_3 + H\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3 + H\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}H$$

8.32 Limonen, portakal ve limon yağında bulunan bir bileşiktir. Limonen, aşırı hidrojen ve bir platin katalizörle etkileştirildiğinde tepkimenin ürünü 1-izopropil-4-metilsikloheksandır. Limonen önce ozon sonra çinko ve suyla etkileştirildiğinde, tepkimenin ürünleri HCHO ve aşağıdaki bileşiktir. Limonenin yapı formülünü yazınız.



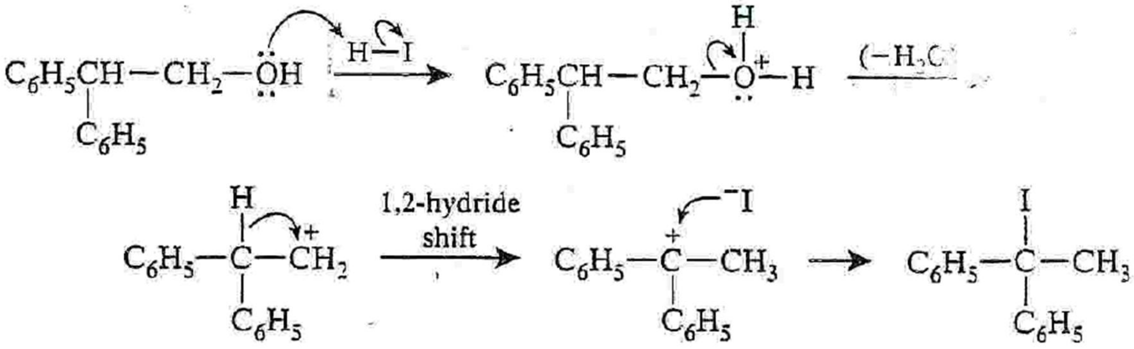
8.32



Limonene

8.33 2,2-Difenil-1-etanol sulu HI ile etkileştirildiğinde tepkimenin ana ürünü 1-iyodo-1,1-difeniletandır. Bu bileşiğin durumu için olası bir mekanizma öneriniz.

8.33

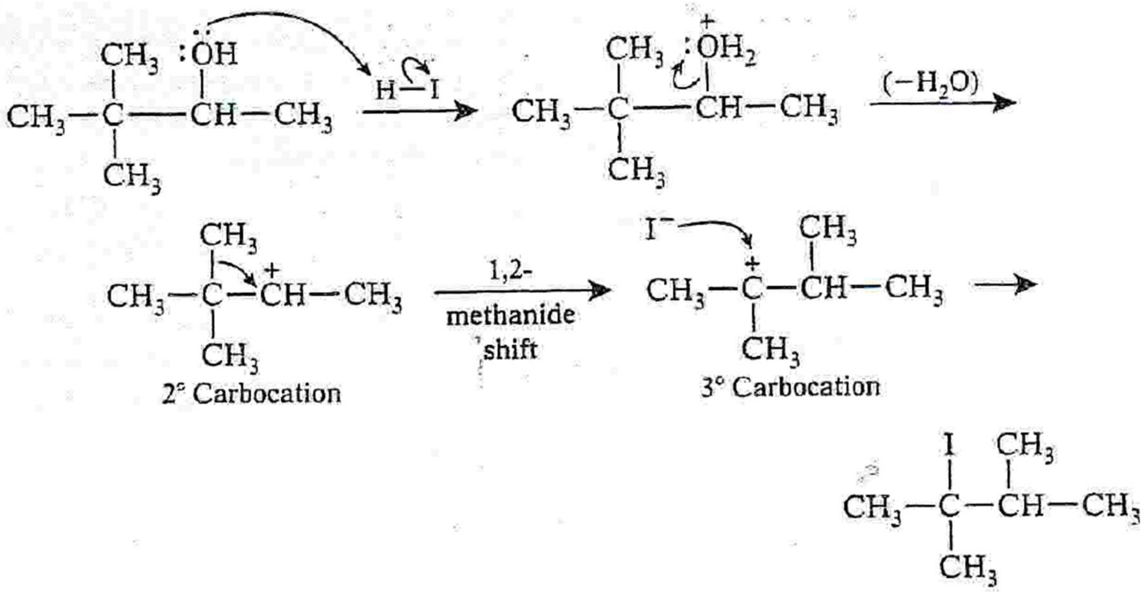


$$C_6H_5\underset{\substack{|\\C_6H_5}}{C}H-CH_2-\ddot{O}H \xrightarrow{H-I} C_6H_5\underset{\substack{|\\C_6H_5}}{C}H-CH_2-\overset{\substack{H\\|}}{\ddot{O}^+}-H \xrightarrow{(-H_2C}$$

$$C_6H_5-\underset{\substack{|\\C_6H_5}}{\overset{\substack{H\\|}}{C}}-\overset{+}{C}H_2 \xrightarrow[\text{shift}]{\text{1,2-hydride}} C_6H_5-\underset{\substack{|\\C_6H_5}}{\overset{+}{C}}-CH_3 \xrightarrow{{}^-I} C_6H_5-\underset{\substack{|\\C_6H_5}}{\overset{\substack{I\\|}}{C}}-CH_3$$

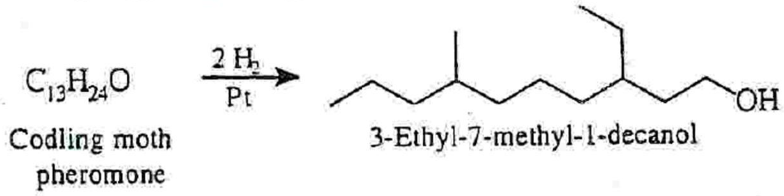
8.34 3,3-Dimetil-2-bütanol derişik HI ile etkileştirildiğinde bir çevrilme meydana gelir. Bu tepkimeden hangi alkil iyodürün oluşacağını umuyorsunuz? (Bu tepkimenin mekanizmasını gösteriniz.)

8.34

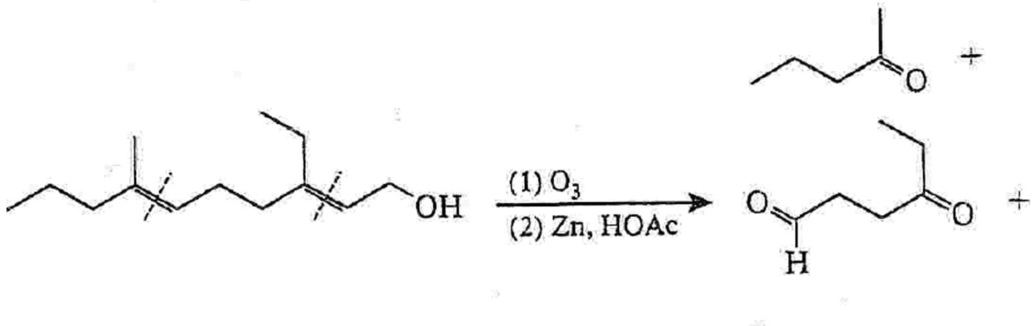


8.35 Feromonlar (Altbölüm 4.16), hayvanlar (özellikle böcekler) tarafından salgılanan maddelerdir ve aynı türlerin diğer üyelerinde özel bir davranış tepkisi oluştururlar. Feromonlar çok düşük derişimlerde bile etkilidirler ve sekse çekici, uyarıcı maddeler ile "bir araya toplayıcı" maddeler içerirler. Meyva kurdunun sekse çekici feromonunun molekül formülü $C_{13}H_{24}O$'dur. Bu feromon, katalitik hidrojenlemeyle iki eşdeğer mol hidrojen soğurur ve 3-etil-7-metil-1-dekanole dönüşür. Bu bileşik, önce ozon ardından da çinko ve suyla etkileştirildiğinde, $CH_3CH_2CH_2COCH_3$, $CH_3CH_2COCH_2CH_2CHO$ ve $OHCCH_2OH$ oluşturur. **(a)** İkili bağların stereokimyasını ihmal ederek, bu feromon için genel bir yapı yazınız. **(b)** İkili bağların (elde edilen diğer kanıtlardan), (2*Z*,6*E*) olduğu bilinmektedir. Meyva kurdunun seks çekicisi için bir stereokimyasal formül yazınız.

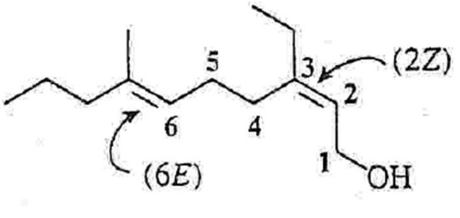
8.35 (a) The hydrogenation experiment discloses the carbon skeleton of the pheromone.



The ozonolysis experiment allows us to locate the position of the double bonds.

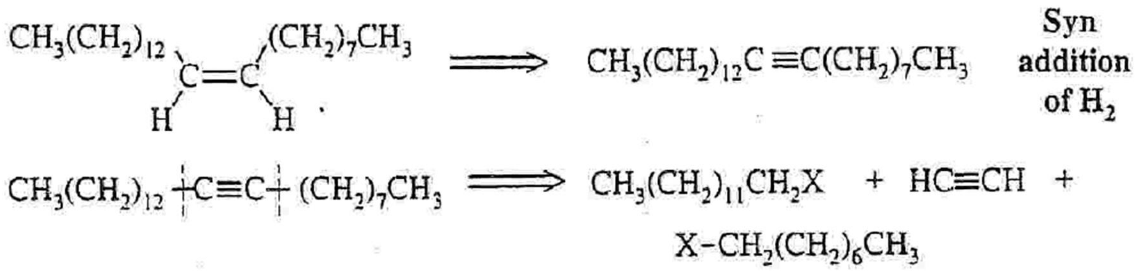


(b)



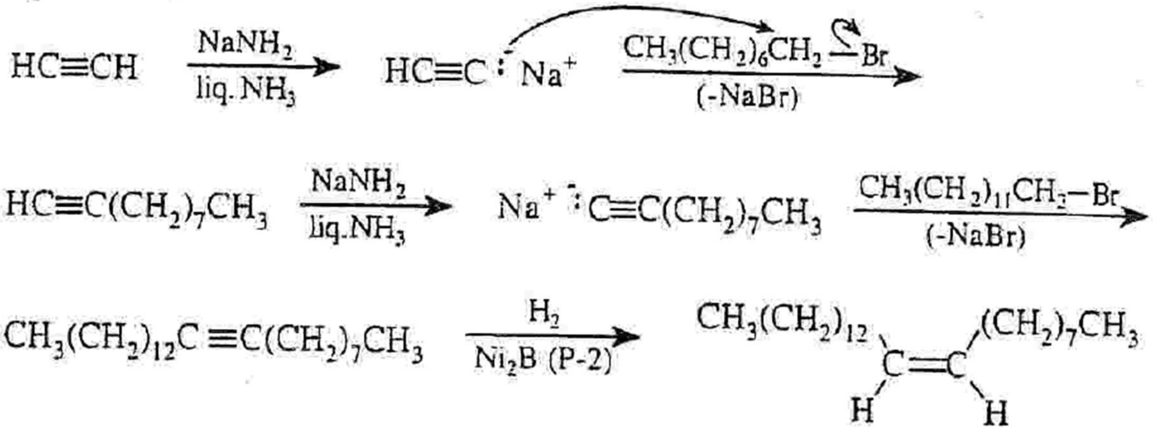
8.36 Yaygın olarak bulunan karasineğin (*Musca domestica*) seks çekicisi muskalur olarak adlandırılan bir bileşiktir. Muskalurun yapısı, (*Z*) $CH_3(CH_2)_{12}CH{=}CH(CH_2)_7CH_3$'tür. Etin ve diğer gerekli reaktiflerle başlayarak muskalur için mümkün olabilecek bir sentez tasarlayınız.

8.36 ***Retrosynthetic analysis***



$$CH_3(CH_2)_{12}\text{–}C{\equiv}C\text{–}(CH_2)_7CH_3 \Longrightarrow CH_3(CH_2)_{11}CH_2X + HC{\equiv}CH + X\text{–}CH_2(CH_2)_6CH_3$$

Synthesis



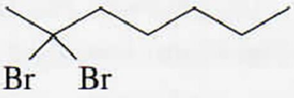
$$HC{\equiv}CH \xrightarrow[\text{liq. }NH_3]{NaNH_2} HC{\equiv}C{:}^- Na^+ \xrightarrow[(-NaBr)]{CH_3(CH_2)_6CH_2\text{–}Br}$$

$$HC{\equiv}C(CH_2)_7CH_3 \xrightarrow[\text{liq. }NH_3]{NaNH_2} Na^+\,{:}^-C{\equiv}C(CH_2)_7CH_3 \xrightarrow[(-NaBr)]{CH_3(CH_2)_{11}CH_2\text{–}Br}$$

$$CH_3(CH_2)_{12}C{\equiv}C(CH_2)_7CH_3 \xrightarrow[Ni_2B\ (P\text{-}2)]{H_2}$$

Muscalure

***8.37** Organik reaktifler olarak (çözücüler hariç) yalnızca etin ve 1-bromopentandan çıkarak ve gerekli olabilecek diğer inorganik bileşikleri kullanarak aşağıda gösterilen bileşik için bir sentez tasarlayınız.

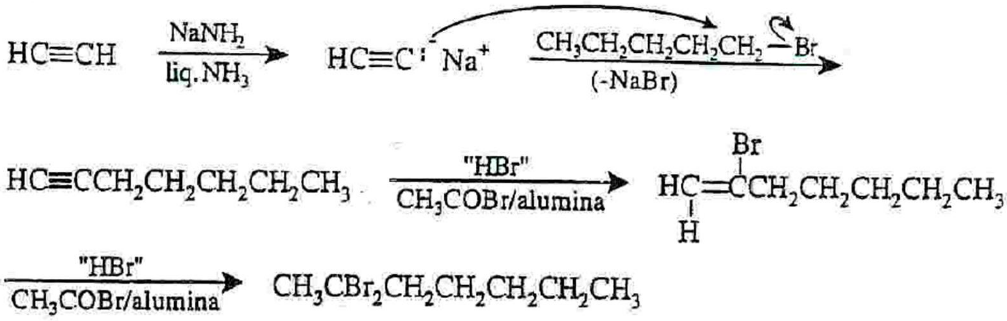


*8.37 *Retrosynthetic analysis*

$$CH_3CBr_2CH_2CH_2CH_2CH_2CH_3 \xRightarrow[\text{nikov addition}]{\text{Markov-}} CH_2{=}CBrCH_2CH_2CH_2CH_2CH_3 + HBr$$

$$\xRightarrow[\text{nikov addition}]{\text{Markov-}} \underset{+\ HBr}{HC{\equiv}CCH_2CH_2CH_2CH_2CH_3} \Longrightarrow HC{\equiv}CH + BrCH_2CH_2CH_2CH_2CH_3$$

Synthesis

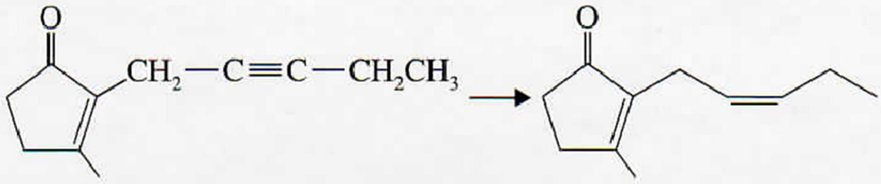


$$HC{\equiv}CH \xrightarrow[\text{liq.}NH_3]{NaNH_2} HC{\equiv}C{:}^-\ Na^+ \xrightarrow[(\text{-}NaBr)]{CH_3CH_2CH_2CH_2CH_2-Br}$$

$$HC{\equiv}CCH_2CH_2CH_2CH_2CH_3 \xrightarrow[CH_3COBr/\text{alumina}]{\text{"HBr"}} \underset{H}{HC}{=}\overset{Br}{C}CH_2CH_2CH_2CH_2CH_3$$

$$\xrightarrow[CH_3COBr/\text{alumina}]{\text{"HBr"}} CH_3CBr_2CH_2CH_2CH_2CH_2CH_3$$

8.38 Aşağıda gösterilen tepkime, önemli bir parfüm bileşeni olan *cis*-jasmonun sentezinde son basamaktır. Bu son basamağı gerçekleştirmek için hangi reaktifleri seçerdiniz?

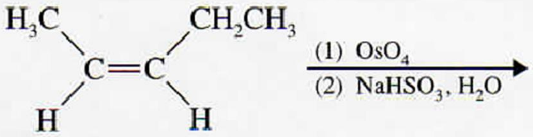


***cis*-Jasmon**

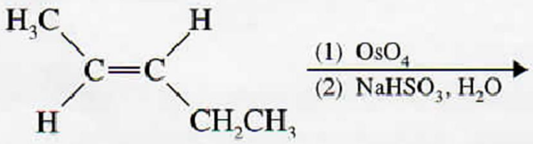
8.38 Syn hydrogenation of the triple bond is required. So use H_2 and $Ni_2B(P\text{-}2)$ or H_2 and Lindlar's catalyst.

8.39 Aşağıdaki tepkimelerin her birinden beklediğiniz ürünlerin tümü için stereokimyasal formüllerini yazınız (Modeller yararlı olabilir).

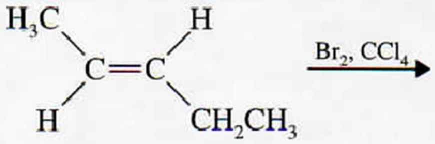
(a)



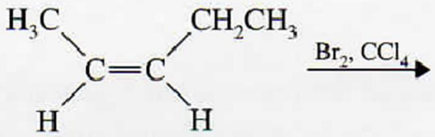
(b)



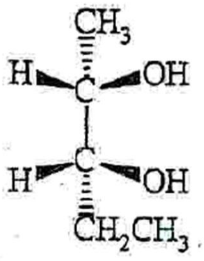
(c)



(d)

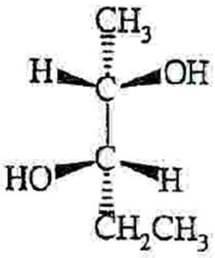


8.39 (a)



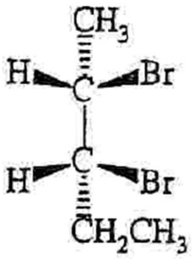
and enantiomer through syn addition

(b)



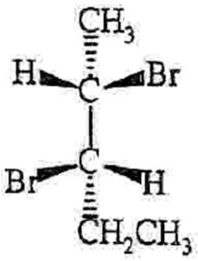
and enantiomer through syn addition

(c)



and enantiomer through anti addition

(d)



and enantiomer through anti addition

8.40 Problem 8.39'a cevap olarak verilen her bir değişik bileşik için (*R*–*S*) tanımlarını belirtiniz.

8.40 (a) (2*S*,3*R*)- [the enantiomer is (2*R*,3*S*)-]

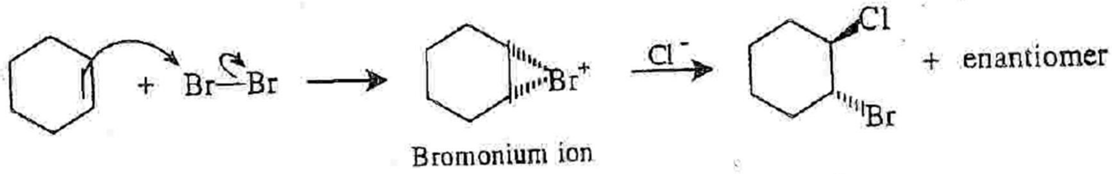
(b) (2*S*,3*S*)- [the enantiomer is (2*R*,3*R*)-]

(c) (2*S*,3*R*)- [the enantiomer is (2*R*,3*S*)-]

(d) (2*S*,3*S*)- [the enantiomer is (2*R*,3*R*)-]

8.41 Sikloheksen, bir sulu sodyum klorür çözeltisi içerisinde bromla tepkimeye sokulduğunda ürünler, *trans*-1,2-dibromosikloheksan, *trans*-2-bromosikloheksanol ve *trans*-1-bromo-2-klorosikloheksandır. Bu son ürünün oluşumunu açıklayan uygun bir mekanizma yazınız.

8.41



The bromonium ion reacts with a chloride ion to produce the *trans*-1-bromo-2-chlorocyclohexane enantiomers.

8.42 Aşağıdaki bileşik çiftlerinin üyelerini birbirinden ayırt etmekte kullanabileceğiniz İR spektrumlarındaki özellikleri öneriniz.

(a) Pentan ve 1-pentin
(b) Pentan ve 1-penten
(c) 1-Penten ve 1-pentin
(d) Pentan ve 1-bromopentan
(e) 2-Pentin ve 1-pentin
(f) 1-Penten ve 1-pentanol
(g) Pentan ve 1-pentanol
(h) 1-Bromo-2-penten ve 1-bromopentan
(i) 1-Pentanol ve 2-penten-1-ol

8.42 (a) 1-Pentyne has IR absorption at about 3300 cm^{-1} due to its terminal triple bond. Pentane does not absorb in that region.

(b) 1-Pentene absorbs in the 1620–1680 cm^{-1} region due to the alkene function. Pentane does not exhibit absorption in that region.

(c) See parts (a) and (b).

(d) 1-Bromopentane shows C-Br absorption in the 690-515 cm^{-1} region while pentane does not.

(e) For 1-pentyne, see (a). The interior triple bond of 2-pentyne gives relatively weak absorption in the 2100–2260 cm^{-1} region.

(f) For 1-pentene, see (b). 1-Pentanol has a broad absorption band in the 3200–3550 cm^{-1} region.

(g) See (f)

(h) 1-Bromo-2-pentene has double bond absorption in the 1620–1680 cm^{-1} region which 1-bromopentane lacks.

(i) 2-Penten-1-ol has double bond absorption in the 1620–1680 cm^{-1} region not found in 1-pentanol.

8.43 Tetrakloroetenin ikili bağının, brom/karbon tetraklorür içerisindeki doymamışlık, testi belirgin değildir. Bu davranış için mantıklı bir açıklama yapınız.

8.43 Because of the electron-withdrawing nature of chlorine, the electron density at the double bond is greatly reduced and attack by the electrophilic bromine does not occur.

***8.44** **A, B** ve **C** bileşiklerinin tümü C_6H_{10} formülüne sahiptir. Üç bileşiğin hepsi soğuk derişik sülfirik asit içerisinde çözünür ve CCl_4 içerisinde bromun rengini hızla giderir. **A** bileşiği, IR spektrumunda yaklaşık 3300 cm^{-1}'de bir soğurmaya sahiptir, fakat **B** ve **C** bileşiklerinin orada bir soğurması yoktur. **A** ve **B** bileşiklerinin her ikisi de, bir platin katalizörü varlığında aşırı hidrojenle etkileştirildiğinde heksan verirler. Bu koşullar altında, **(C)** bileşiği yalnızca bir eşdeğer mol hidrojen soğurur ve C_6H_{12} formülüne sahip bir bileşik verir. **A** bileşiği sıcakta bazik potasyum permanganat ile yükseltgendikten sonra oluşan çözelti asitlendirildiğinde izole edilen tek ürün, $CH_3(CH_3)_3CO_2H$'dir. **(B)** bileşiğinin benzer yükseltgenmesi yalnız $CH_3CH_2CO_2H$ verirken **C** bileşiğinin benzer şekilde etkileştirilmesi ise yalnız $HO_2C(CH_2)_4CO_2H$ verir. **A, B,** ve **C** bileşiklerinin yapıları nasıldır?

*8.44 The index of hydrogen deficiency of **A, B,** and **C** is two.

$$\begin{array}{l} C_6H_{14} \\ \underline{C_6H_{10}} \\ \quad H_4 \;=\; \text{2 pairs of hydrogen atoms} \end{array}$$

This result suggests the presence of a triple bond, two double bonds, a double bond and a ring, or two rings. The fact that **A, B,** and **C** all decolorize Br_2/CCl_4 and dissolve in concd. H_2SO_4 suggests they all have a carbon-carbon multiple bond.

A must be a terminal alkyne, because of IR absorption at about 3300 cm^{-1}.

Since A gives hexane on catalytic hydrogenation, A must be 1-hexyne.

$$\underset{\textbf{A}}{CH_3(CH_2)_3C{\equiv}CH} \xrightarrow[Pt]{2\,H_2} CH_3(CH_2)_4CH_3$$

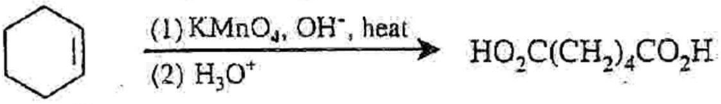
This is confirmed by the oxidation experiment

$$CH_3(CH_2)_3C{\equiv}CH \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ heat} CH_3(CH_2)_3CO_2H \ + \ CO_2\uparrow$$

Hydrogenation of **B** to hexane shows that its chain is unbranched, and the oxidation experiment shows that **B** is 3-hexyne.

$$\underset{\textbf{B}}{CH_3CH_2C{\equiv}CCH_2CH_3} \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ heat} 2\ CH_3CH_2CO_2H$$

Oxidation of **C** shows that it is cyclohexene.

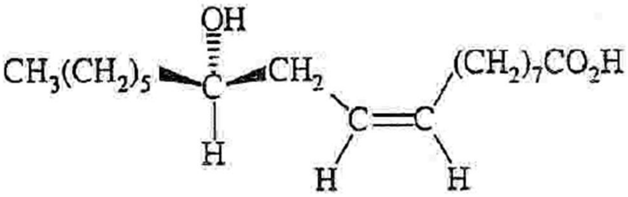


C

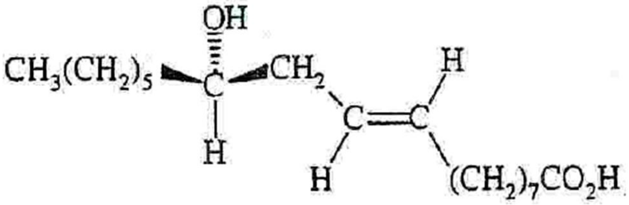
8.45 Risinoleik asit, $CH_3(CH_2)_5CHOHCH{=}CH(CH_2)_7CO_2H$ yapısına sahip hintyağından izole edilen bir bileşiktir. **(a)** Bu yapının kaç tane stereoizomeri mümkündür? **(b)** Bu yapıları yazınız.

8.45 (a) Four

(b)



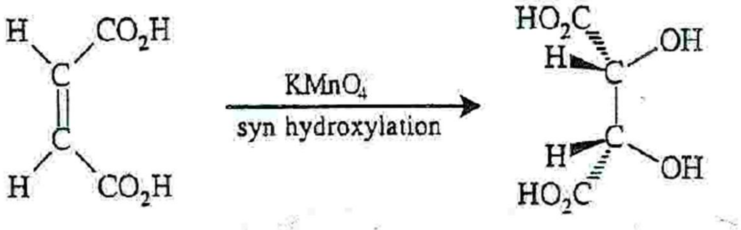
+ enantiomer



+ enantiomer

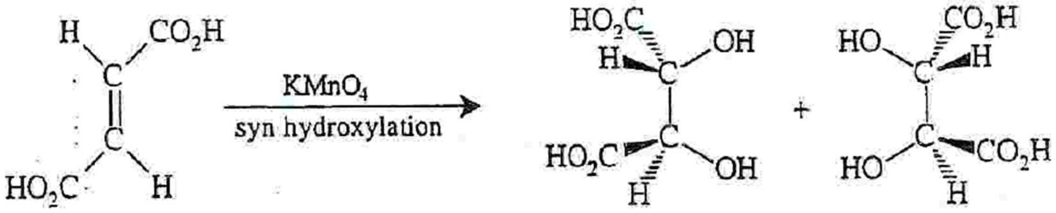
8.46 $HO_2CCH{=}CHCO_2H$ genel formülüne sahip iki dikarboksilik asit vardır. Bu karboksilik asitlerden biri maleik asit, diğeri ise fumarik asit olarak adlandırılır. Kekulé, 1880 yılında, soğuk seyreltik $KMnO_4$ ile etkileştirildiğinde maleik asitin *mezo*-tartarik asit, fumarik asitin ise (±)-tartarik asit verdiğini bulmuştur. Bu bilgilerin maleik asit ve fumarik asitin stereokimyasal formüllerini yazmada nasıl kullanıldığını gösteriniz.

8.46 Hydroxylations by $KMnO_4$ are syn hydroxylations (cf. Section 8.9). Thus, maleic acid must be the *cis*-dicarboxylic acid:



Maleic acid *meso*-Tartaric acid

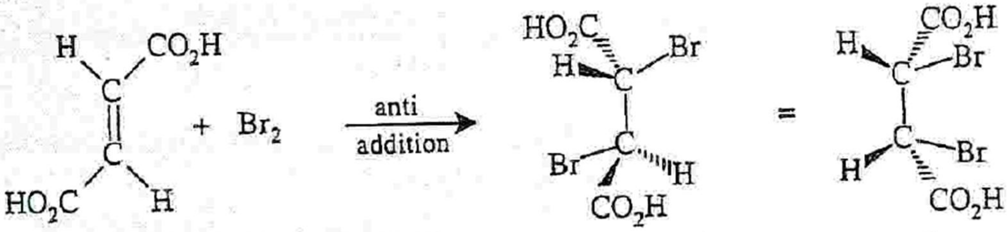
Fumaric acid must be the *trans*-dicarboxylic acid:



Fumaric acid (±)-Tartaric acid

8.47 Maleik asit ve fumarik asite brom katılmasının stereokimyasal sonuçlarını tahmin etmek için bir önceki probleme verdiğiniz cevabı kullanınız. (**a**) Hangi dikarboksilik asit brom katarak bir mezo bileşiği verir? (**b**) Hangisi bir rasemik yapı oluşturur?

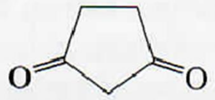
8.47 (a) The addition of bromine is an anti addition. Thus, fumaric acid yields a meso compound.



A meso compound

(b) Maleic acid adds bromine to yield a racemic modification.

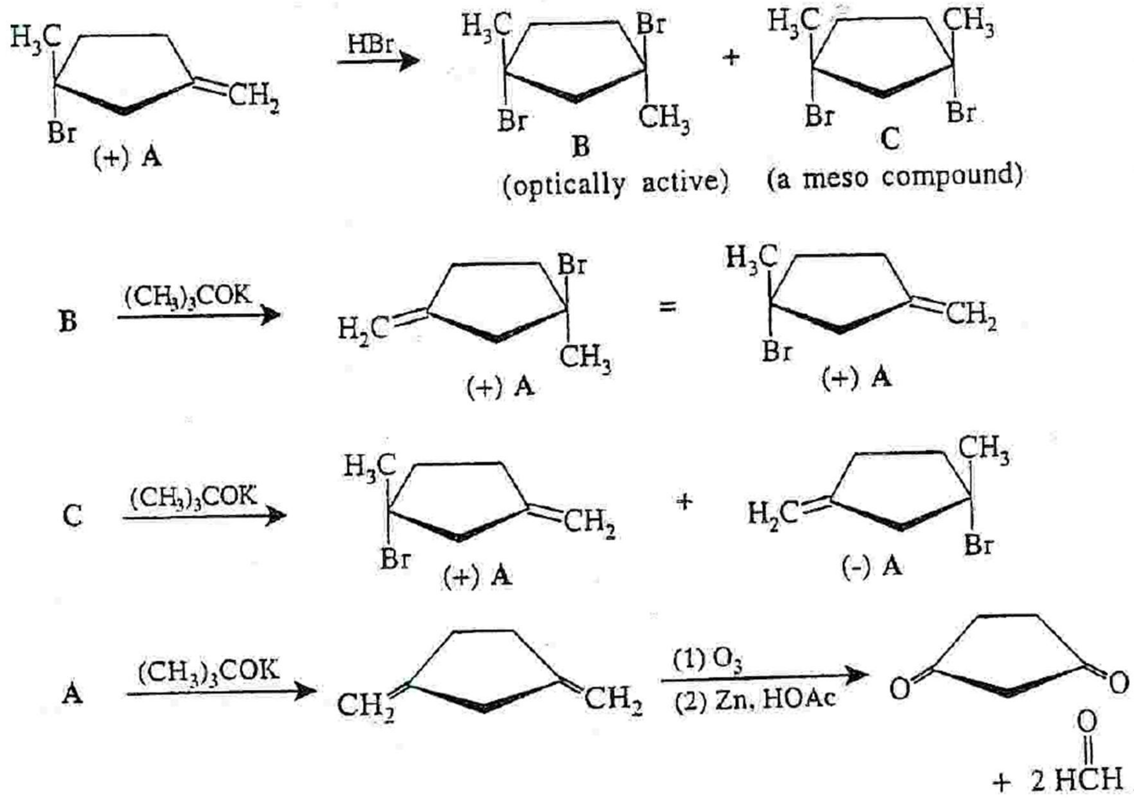
8.48 Optikçe aktif bir bileşik olan **A** (bu bileşiğin dekstrorotatori olduğunu varsayınız) $C_7H_{11}Br$ molekül formülüne sahiptir. **A** bileşiği, peroksitsiz ortamda hidrojen bromür ile tepkime vererek $C_7H_{12}Br_2$ molekül formülüne sahip **B** ve **C** izomerik ürünlerini verir. **B** bileşiği optikçe aktif, **C** ise optikçe aktif değildir. **B**'nin bir mol potasyum *ter*-bütoksit ile etkileştirilmesiyle (+)-**A** oluşur. **C** bir mol potasyum *ter*-bütoksit ile etkileştirilirse **D** (C_7H_{10}) oluşur. Bir mol (**D**), önce ozon ile ardından çinko ve asetik asit ile etkileştirilirse 2 mol formaldehit ve 1 mol 1,3-siklopentandion oluşur.



1,3-Siklopentandion

A, B, C ve **D** için streokimyasal formülleri öneriniz ve bu dönüşümlerin içerdiği tepkimeleri yazınız.

*8.48

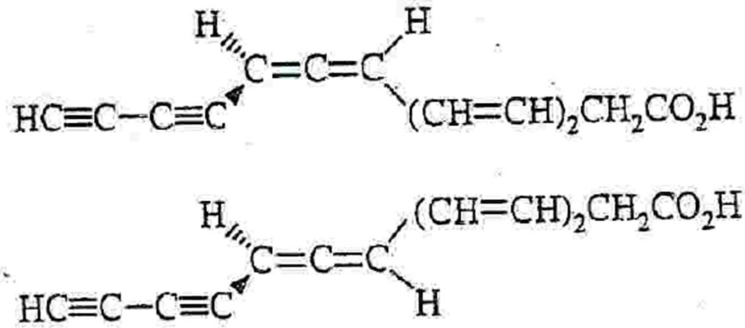


8.49 Kikomisin olarak adlandırılan doğal olarak bulunan bir antibiyotik, aşağıdaki formüle sahiptir. Mikomisin, optikçe aktiftir. Mikomisinin enantiyomerik şekillerini yazarak bunu açıklayınız.

$$HC\equiv C-C\equiv C-CH=C=CH-(CH=CH)_2CH_2CO_2H$$

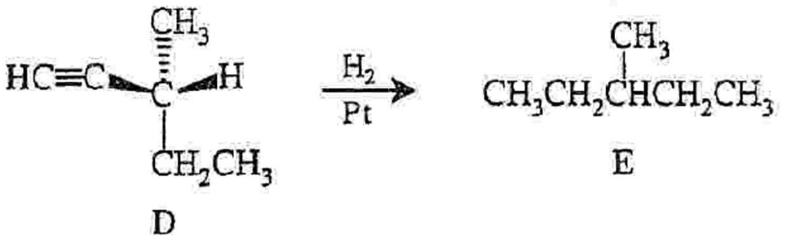
Mikomisin

8.49



8.50 Optikçe aktif bir bileşik olan **D**, C_6H_{10} formülüne sahiptir ve İR spektumunda yaklaşık 3300 cm^{-1}'de bir pik verir. **D**, katalitik hidrojenleme ile **E** (C_6H_{14})'yi oluşturur. **E** bileşiği optikçe aktif değildir ve yarılamaz. **D** ve **E** bileşiklerinin yapılarını öneriniz.

8.50



Optically active
(the other enantiomer is
an equally valid answer)

Optically inactive
(nonresolvable)

8.51 (**a**) Alkenlere brom katılması mekanizmasının benzerini uygulayarak **A**, **B** ve **C**'nin muhtemel üç boyutlu yapılarını çiziniz.

Siklopentenin bromla tepkimesi **A**'yı verir.

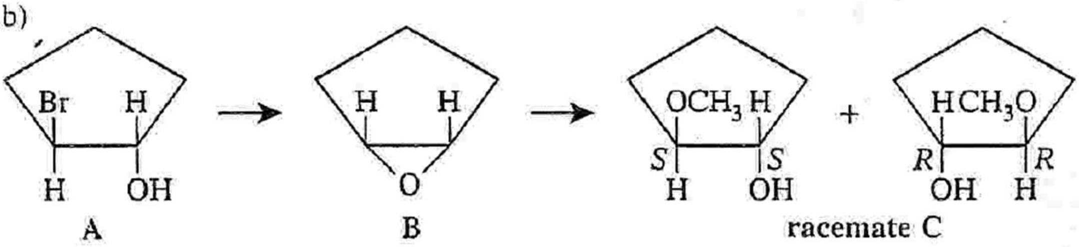
A'nın sulu NaOH (1 eşdeğer, soğuk) ile tepkimesi **B**'yi, C_5H_8O verir (3590-3650 cm^{-1}'de infared soğurması yoktur). (Bir ipucu için skulenin halkalanmasındaki tartışmaya bakınız.)

B'nin katalitik miktarda kuvvetli bir asit içeren metanol içerisinde ısıtılması, 3590-3650 cm^{-1}'de infrared soğurması yapan **C**'yi, $C_6H_{12}O_2$, verir.

(**b**) **C** bileşiği için tahmin ettiğiniz yapılardaki stereomerkezlerin *R* ve *S* konfigürasyonlarını belirleyiniz. Bu bileşik, tek bir stereoizomer olarak mı yoksa bir rasemat olarak mı oluşur.

(**c**) C'nin stereokimyası hakkındaki tahminlerinizi deneysel olarak nasıl doğrularsınız?

*8.51 (a,b)



(c) C, in contrast to its *cis* isomer, would exhibit no intramolecular hydrogen-bonding. This would be proven by the absence of infrared absorption in the 3500- to 3600-cm^{-1} region when studied as a very dilute solution in CCl_4. C would only show free O—H stretch at about 3625 cm^{-1}

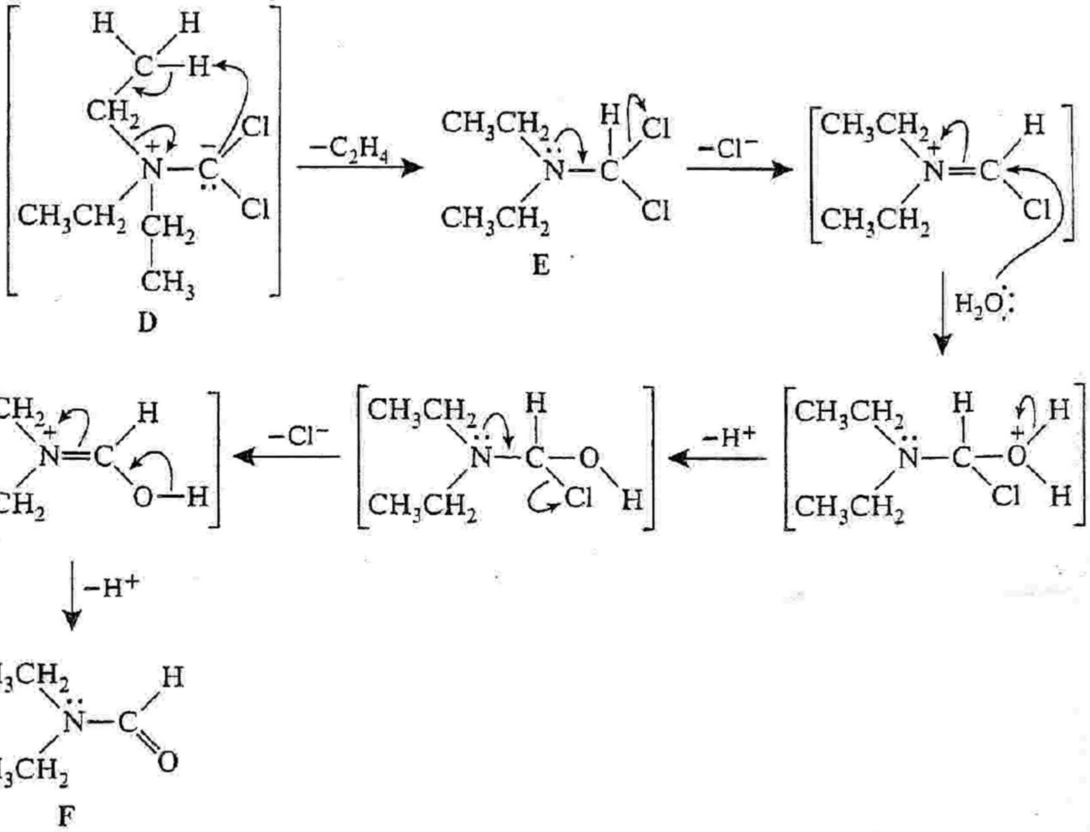
***8.52** Trietilamin, $(C_2H_5)_3N$, tüm aminlerde olduğu gibi ortaklaşılmamış bir elektron çiftine sahip azot atomu bulundurur. Diklorokarben molekülü de ortaklaşılmamış bir elektron çiftine sahiptir. Bunların her ikisi de aşağıdaki gibi gösterilebilir. **D**, **E** ve **F** bileşiklerinin yapılarını çiziniz.

$(C_2H_5)_3N: + :CCl_2 \longrightarrow$ **D** (kararsız bir katılma ürünü)

D $\longrightarrow$ **E** $+ C_2H_4$ (molekül içi bir E_2 tepkimesiyle)

E $\xrightarrow{H_2O}$ **F** (Su, ikiz dihalojenürleri elde etmek için kullanılanın tersi bir yer değiştirme verir.)

*8.52



Radikal Tepkimeleri